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JOURNAL OF CHEMICAL EDUCATION

for April, 1936

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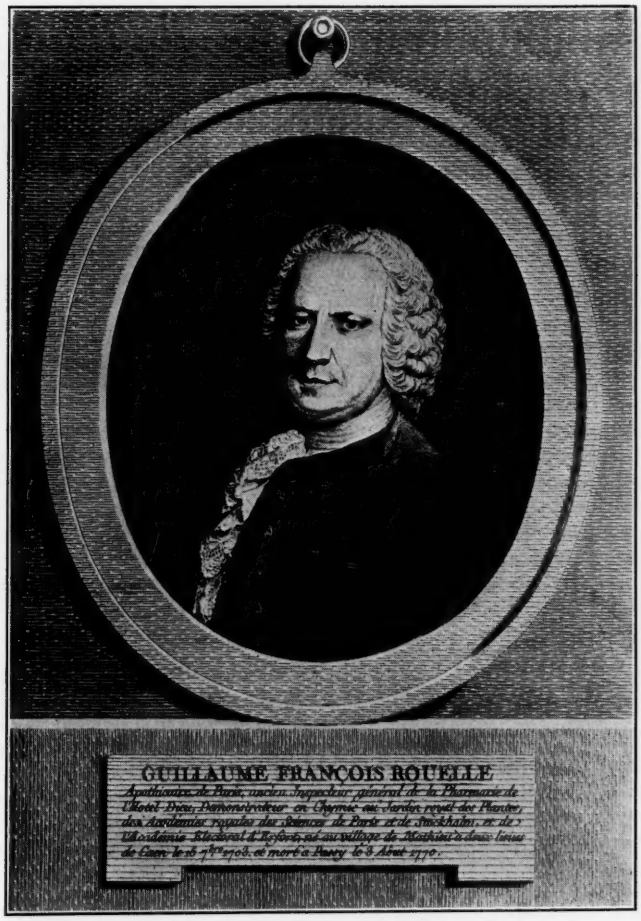

GUILLAUME-FRANCOIS ROUELLE (1703–1770)

Teacher of Lavoisier and Proust. Pharmacist and *démonstrateur* at the Jardin du Roi. He was an exceptionally able manipulator and accompanied his demonstrations by brilliant lectures which wholly eclipsed those of Bourdelin, who was professor by title. He was the first to recognize that salts are produced by the combination of acids and bases. He isolated urea from urine and is credited with the discovery of sulfuretted hydrogen and of a number of other substances. (*Contributed by Tenney L. Davis.*)

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EDITOR'S OUTLOOK

ESSENTIALS OF HIGH-SCHOOL CHEMISTRY. Judging by the many inquiries concerning the "high-school chemistry outline," and the many requests for reprints of the Correlation Committee's previous report, that have reached this office during the past year, the Outline of Essentials presented on pages 175–9 of this number meets a real need, and will be greeted with widespread interest. We regret that space limitations have prevented us from making this report available sooner. As it is, we have given the outline precedence over many manuscripts of earlier acceptance dates in the hope that the evident demand for it and the desirability of its timely appearance might justify us to authors whose papers still await publication.

It seems worthy of emphasis that the present outline, like its predecessor, is based upon first-hand acquaintance with the problems and objectives of the secondary school. Two members of the committee of four are actively engaged in secondary-school instruction and at least one of the other members has high-school teaching experience. The report, then, does not by any means embody an attempt to impose the college viewpoint upon secondary-school instructors, nor to build the secondary-school course around college-entrance requirements, without regard to the needs of the majority of secondary-school students who never enter college. Further aspects of the committee's attitude and aims are developed in its introductory statement.

Perhaps a word regarding the unitized form of the outline should be added. The committee has attempted to organize the topics of its outline in a manner adapted to the unit method of presentation. No teacher should assume, however, that the mere adoption of a "unitized" outline automatically leads to teaching by the unit method.

The first modern statement of the nature of a learning unit is attributed to Professor H. C. Morrison ("The practice of teaching in the secondary school," 1926). The principles suggested by Professor Morrison have been summarized essentially as follows:

1. A unit in science should present an important essential aspect of the environment and explain a number of related, subordinate aspects which contribute to the central idea.

2. A unit must contribute to understanding rather than give a descriptive account.

3. When learned, a unit should result in a new understanding of such nature that it will permanently modify the pupil's attitude and affect his behavior.

As a convenient check upon "the real unity of a unit," the following questions have been suggested:

1. Does each major division of the unit bring out an idea which is clearly focused on the idea expressed in the unit title, or on the solution of the question asked by the title?

2. If the unit is divided into problems, do these problems take up subordinate aspects of the unit idea, or are they merely topics from the old organization when expressed in declarative, rather than question, form?

Although the suggested check questions seem to lay emphasis on the outline itself, a little reflection suffices to reveal that the essential nature of the course inheres, to a considerable extent, in the teacher's method of presentation. If, to the teacher, unitization means merely segmentation of subject matter; if, to the student, it is permitted to mean that a succession of quizzes may be passed and forgotten—the entire point of the unit method has been missed.

THE SHORTAGE (?) OF COMPETENT CHEMISTS. Rumors to the effect that a shortage of competent chemists is upon us, or impends in the near future, are beginning to circulate. This is interesting and, in one sense, encouraging, if true. We would suggest, however, that vocational advisers subject this rumor to critical investigation before accepting it as a basis for the recommendation that more students select chemistry as a professional career.

Although we are not in a position to collect complete and detailed data on chemical unemployment, the apparently reliable reports available to us indicate that there are still *competent* chemists unemployed or unsuitably employed. At present we could conscientiously endorse the aforesaid rumor only to the extent of saying that there is a considerable shortage of five- or six-thousand-dollar-a-year men to be hired at two or three thousand dollars a year.

The cover picture is a reproduction of one of the more fanciful of the conceptions of David Teniers the younger—"Alchymistenwerkstatt." We are indebted to Dr. Ralph E. Oesper for the photograph.

FRANÇOIS-MARIE RAOULT MASTER CRYOSCOPIST

FREDERICK H. GETMAN

Hillside Laboratory, Stamford, Connecticut

WHILE the name of François-Marie Raoult is associated in the minds of most students of chemistry with the law which bears his name and with the early developments of the theory of solutions, it is probably true that relatively few are aware of his remarkable achievements in the realm of precise cryoscopy. Very soon after undertaking to measure the freezing points of solutions, Raoult recognized that the experimental methods which had been developed by Rüdorff, de Coppet, and Beckmann left much to be desired. While these methods served quite satisfactorily for the routine determination of molecular weights, where a fairly large depression of the freezing point of the solvent could be obtained, Raoult became convinced that an apparatus capable of greater precision was absolutely essential for his projected experiments with dilute solutions.

After making a detailed study of the various sources of error involved in the measurement of freezing points, Raoult undertook the construction of a piece of apparatus which he designated as a "cryoscope of precision." A diagram of this apparatus is shown in Figure 1. It consisted of a glass vessel *B*, hermetically closed with a lid of copper; attached to this cover was a copper muffle which reached nearly to the bottom of *B* and within which was placed the freezing-tube *C*. The vessel *B* was filled with ether through which a current of dry air could be bubbled by means of an aspirator *p*. A brass tube bent into the form of a ring and perforated with a series of holes served to admit and distribute the air through the ether in *B*. By proper regulation of the velocity of the current of air it was possible to control the degree of cooling. If it was desired to raise the temperature in *C*, it was only necessary to transfer some ether from the vessel *D* by compressing the rubber bulb *E*. The excess of ether from *B* was collected in the vessel *A*. With this relatively simple arrangement Raoult was able to maintain any temperature he desired between that of the room and −15°C. In order to insure greater thermal insulation of the apparatus Raoult surrounded *B* with a heavy jacket of felt. The consumption of ether was relatively small, one liter sufficing for ten hours of continuous operation. The liquid in the freezing tube *C* was efficiently stirred by means of a spiral stirrer constructed of platinum foil which was attached to the thermometer by means of platinum wires. The upper portion of the thermometer was passed through a stopper inserted in the center of the horizontal wheel

FIGURE 1.—RAOULT'S "CRYOSCOPE OF PRECISION"

of a pair of beveled gears, the latter being rotated by means of a small water turbine at the rate of 180 to 300 revolutions per minute.

In carrying out freezing-point determinations with this apparatus Raoult exercised extreme precaution to secure results of a very high order of accuracy. In order to minimize changes in concentration due to supercooling he systematically inoculated the solution in the freezing tube with a minute fragment of ice, thereby limiting supercooling to 0.5°. He made a thorough study of the influence of the temperature of the environment on the freezing point of a solution and derived a simple mathematical expression for the calculation of the true from the apparent freezing temperature. In this connection it is interesting to observe that in this investigation he fully confirmed the conclusions previously reached by Nernst and Abegg concerning the convergence temperature. Furthermore, Raoult took into consideration errors arising from the formation of a sheath of ice on the walls of the freezing tube as well as from the heat developed by the agitation of the solution by the stirrer. It is hardly necessary to mention that the usual corrections involved in precise measurements of temperature with a mercury thermometer were applied throughout his cryoscopic investigations. The influence of dissolved air on the freezing point was also studied with the result that Raoult found that the lowering of the freezing point of pure water, saturated with air at 0°, is not more than 0.002°, and that if one employs water which has been distilled for a sufficient time to permit of saturation with air no appreciable error is introduced, provided the same sample of water is used in the preparation of the solutions. A detailed summary of these and other corrections was published by Raoult in a

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paper treating of the sources of error in precise cryoscopic measurements. The accompanying illustration,* Figure 2, is taken from a hitherto unpublished photograph of Raoult in his laboratory at Grenoble:

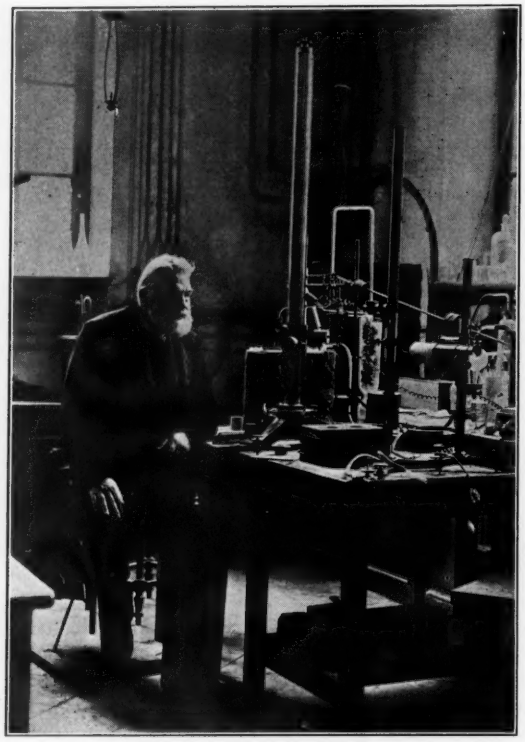


FIGURE 2.—RAOULT IN HIS LABORATORY AT GRENOBLE

on the table beside which he is seated may be seen the "cryoscope de précision" previously described. Although the thermometer employed by Raoult was made by the celebrated Baudin of Paris, evidently the latter did not approve of the type specified by Raoult for his particular work, as appears from the following incident related by van't Hoff. Happening to be in Paris, van't Hoff paid a visit to the shop of the famous mechanician and asked Baudin to supply him with an exact replica of Raoult's thermometer. Baudin strongly advised him against this, remarking, "The thermometer which M. Raoult uses is 'antediluvian!'" But, as van't Hoff adds, "Nevertheless with this 'antediluvian' thermometer the world was conquered."

In order to appreciate the high degree of accuracy attained by Raoult in his cryoscopic measurements one need but compare his results with the data given in the *International Critical Tables*, which may be accepted as the best available data in this field. Such a comparison is given in the following table for four different solutes taken at random from Raoult's papers.

Solute	*Concentration*	*f(Raoult)*	*f(I. C. T.)*
Sucrose	0.003	0.0053°	0.0056°
Ethyl alcohol	0.026	0.0476	0.0476
Acetic acid	0.098	1.886	1.890
Sodium chloride	0.001	0.00367	0.00366

Although the introduction of Dewar vacuum vessels, platinum resistance thermometers, thermoelectric couples, and their various accessories, such as Wheatstone bridges and potentiometers, have enabled the modern physical chemist to extend his investigations into the realm of extremely dilute solutions, the degree of accuracy attained by Raoult over the range of concentration embraced by his measurements remains unsurpassed.

The period from 1878 to 1896 was one of intense activity in Raoult's scientific career. During this interval of time he published forty papers on his cryoscopic studies alone which, together with a series of papers treating of his investigations of the vapor pressures of solutions, constitute the major part of his contribution to scientific literature.

In his memorial lecture on Raoult delivered before the Chemical Society in London in 1902, van't Hoff said, "The work on cryoscopy came just at a time when an ardent activity was developing in different countries and from different points of view. Victor Meyer in Germany and Paterno in Italy applied Raoult's method of determining molecular weights as early as 1886; .... then came the theory of solutions, developed by Arrhenius in Sweden and by myself in Holland, and then the great support lent by Ostwald in his *Zeitschrift für physikalische Chemie*, in which Raoult at once took part with enthusiasm.....Rarely has science seen such an international interest centered on one problem, and Raoult stood at once foremost, in the position of advantage belonging to the man who relies on fact in the first instance and is eager for generalization, absolutely independent of his opinions, and open to every achievement on his way."

Raoult was born in 1830 in the small village of Fournes in the northern part of France. His father, who held a subordinate government appointment, arranged for his son to enter the *Bureaux de l'Enregistrement*, but this failed to satisfy the young man's aspirations and he finally persuaded his parents to consent to his plans for the pursuit of his studies in Paris. With very limited means and without influential friends to assist him Raoult entered upon a period of privation and struggle in order to attain the education he so much desired. At the age of 33, however, he obtained the long-coveted degree of *Docteur ès-sciences physiques* from the University of Paris. After holding a succession of appointments at Rheims, Bar-le-Duc, and Sens he eventually joined the faculty of science in the University of Grenoble in 1867 and three years later was promoted to the chair of chemistry in the same institution, a position which he filled with distinction until his death in 1901. A man of retiring disposition, he found his greatest satisfaction in the quiet life of a small university where he could carry on his work free

* The author is indebted to Professor Andrieux of the *Institut d'Électrochimie et d'Électrométallurgie* of the University of Grenoble for the interesting photograph of Raoult.

from distraction. In writing of his life, van't Hoff has pointed out that "He rarely left France, and for the larger part of his life, lived in that somewhat out-of-way town, Grenoble. Raoult's life thus offers little of attractiveness; it is not romantic; yet after many years of work, the romance of his life was that almost sudden rise to fame, spreading from this nearly unknown corner, first over the frontier of his country, and then back to France, which made him one of the most prominent men of science of his age." The career of this retiring and unassuming man strikingly exemplifies the truth of Emerson's words: "If a man can write a better book, preach a better sermon or make a better mouse-trap than his neighbor, though he build his house in the woods, the World will make a beaten path to his door."

In 1889 Raoult was awarded the *Prix International de Chimie LaCaze*, amounting to 10,000 francs, and this was followed three years later by the Davy Medal of the Royal Society. In 1890 he was made *Correspondent de l'Institut* and also honorary Fellow of the Society of Rotterdam, while similar honors were bestowed upon him by the Literary and Philosophical Society of Manchester (1892), the Chemical Society of London (1898), and the Academy of St. Petersburg (1899). In 1895 he received the *Prix de l'Institut* of 20,000 francs, and in 1900 was elected to the post of *Commandeur de la Légion d'Honneur*. Of the many distinctions awarded Raoult the latter was the one which afforded him the greatest satisfaction. Although he had reached, in 1900, the age limit established at Grenoble for the retirement of its professors, Raoult continued to pursue his investigations in the field which he had made his own, and only a short time before his death, in the spring of 1901, he had projected a new series of researches.

The rector of the Academy of Grenoble, N. Boirac, in a memorial address on Raoult, said of him, "*La vie de M. Raoult se résume dans un seul mot: le travail.*" Another of Raoult's biographers has written: "None of those who have been privileged to know him will ever forget his gentle manner, the warmth of his greeting, his absolute fairness or the inspiration of his countenance." It thus appears that Raoult the man was not overshadowed by Raoult the scientist. Whether as organic chemists, inorganic chemists, or physical chemists, we all are debtors to this remarkable man for his contributions to the fundamental principles of our science. It is especially fitting as we approach the fiftieth anniversary of the publication of that series of papers recording the experiments which form the underlying basis of our modern views concerning solutions that we should recall the important part played by Raoult in this work.

TITANIUM *and* ITS MORE USEFUL COMPOUNDS*

ROBERT M. McKINNEY AND WILLARD H. MADSON

Krebs Pigment & Color Corporation, Wilmington, Delaware

The history and occurrence of titanium are briefly outlined.

Some important methods for the detection and the quantitative determination of titanium are given, together with their limitations.

The chemistry of titanium is discussed, with special reference to the properties in the various valences and including the preparation and properties of colloidal hydrous titanium dioxide.

Recent commercial developments of titanium substances are surveyed, with special attention to their production and use; some of the more important materials being titanous sulfate, titanium tetrachloride, titanium dioxide, and titanium alloys.

✦ ✦ ✦ ✦ ✦ ✦

A FEW years after the close of the Revolutionary War, the announcement was made of the discovery of a new element, titanium. For nearly a hundred and fifty years this material has been called rare. A glance at the table of the abundance of the elements in the earth's crust (Table 1) shows that in reality titanium is one of the more abundant elements; furthermore, its occurrence is almost universal. F. W. Clarke of the U. S. Geological Survey found the element in 98% of the 800 igneous rocks analyzed by the Survey.

* Contribution to the symposium on Recent Advances in the Chemistry of the Rarer Elements conducted by the Division of Inorganic and Physical Chemistry at the eighty-ninth meeting of the American Chemical Society, New York, April 25, 1935.

TABLE 1

ABUNDANCE OF THE ELEMENTS IN THE EARTH'S CRUST (BERG)

Element	*% in Earth's Crust*	*Relative Abundance of Titanium*
Fe	5.08	–
Ti	0.63	1
Mn	0.09	7
Zr	0.023	27
Ni	0.018	35
Zn	0.017	37
Cu	0.010	63
Li	0.004	158
Pb	0.003	210
Sn	0.0006	1,050
Be	0.0005	1,260
Ge	0.0001	6,300
Cb	0.00006	10,500
Ta	0.00002	31,500
Ag	0.000006	105,000
Pt	0.000005	126,000
Au	0.0000006	1,050,000
Re	0.0000001	6,300,000

There appear to be two causes for this classification of titanium. First, the element was found in forms which were not easily recognized. Thus, during its early history it was often overlooked and attention was centered upon more easily recognized materials. Secondly, titanium has a very interesting habit of "playing tricks"; often it does not act or react as one would expect. However, we hope and believe that in the near future titanium will be generally recognized as an abundant and important element. It is expected that the element will become equal to or even exceed in importance the less abundant elements such as copper, tin, zinc, and lead. This change will take place as soon as the public realizes the commercial importance of titanium and when the element receives its proper consideration in at least some of the introductory chemistry books. In this brief discussion we hope to indicate the great growth in the importance of titanium in commerce, especially during the last few years.

There are three important classes of titanium ores, namely, rutile, brookite, and ilmenite. The first two have high titanium contents, but due to the lack of economical processes for recovery of titanium in a useful form, and the limited amounts of the ores, they are not mined extensively at the present time. A deposit of rutile occurs in Nelson county, Virginia; brookite deposits are found in Arkansas.

Ilmenite is by far the most important ore of titanium. It occurs as a black beach sand and in massive rock formations. Some beach sands of Florida, India, Africa, Ceylon, and Brazil contain large percentages of ilmenite. The more important massive ilmenite formations are found in Norway and Quebec, with smaller deposits in Virginia and New York. The most extensive mining operations of ilmenite are carried on in India. The ore is shipped to both the United States and Europe for pigment and alloy manufacture. Norwegian ilmenite is also being used by Germany and England.

OXIDES OF TITANIUM

Titanium is in the fourth group of the periodic table and has properties indicative of its position. Several oxides of titanium have been reported, namely, TiO, Ti_2O_3, TiO_2, and TiO_3 or Ti_2O_5. The monoxide of titanium has been reported, but its preparation in a state of purity is very dubious. A few bivalent salts of titanium have been reported and described. There is doubt in the minds of some as to the proved existence of bivalent titanium. In general, very little is known about bivalent titanium and we know of no investigation along this line in recent years.

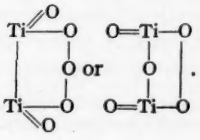
The sesquioxide of titanium has been prepared in a variety of ways. It is isomorphous with hematite and is formed as black lustrous crystals, insoluble in hydrochloric acid or nitric acid, but soluble in sulfuric acid.

Salts of trivalent titanium are easily made by the reduction of the quadrivalent material. They are strong reducing agents and are usually recognized by their violet color in water solutions. They are of commercial value as stripping agents in the dyeing industry, and are also important in analytical chemistry. The uses of trivalent titanium will be discussed later.

The dioxide is the most common and the most stable form of titanium. In the pure state it is a white, dense material with an index of refraction higher than diamond. In nature it is often colored by impurities. It is very easily made from other quadrivalent compounds of titanium. Titanic chloride and sulfate are well known because of their commercial importance. In many cases the properties of other titanic salts are not well known and the list of quadrivalent compounds is far from complete.

Alkali titanates have been prepared by the reaction of TiO_2 with the alkali at elevated temperatures. Barium and lead titanates are on the market at the present time. However, very little is known about the chemistry of titanates.

The addition of hydrogen peroxide to an acid solution of a titanium salt produces a yellow-colored solution. In this form titanium will remain in solution upon the addition of excess alkali. This color reaction is often used for the detection and for the colorimetric determination of titanium. However, since the color forms only with the addition of peroxides or per-salts or -acids, it is thought that the material must have a peroxide structure. A consideration of peroxide structure leads to some interesting speculation. If TiO_3 has the structure , it seems possible that a compound TiO_4 with the structure may exist.

Then, considering another proposed formula, Ti_2O_5, the compound may be considered as a molecular compound of $TiO_2 \cdot TiO_3$, but it is also possible that it has a ring structure such as  or . A large

number of different formulas can be postulated if peroxide groups are substituted for the oxygen atoms attached to the titanium atoms; these compounds would exhibit isomerism and polymerism of inorganic materials.

COLLOIDAL HYDROUS TITANIUM DIOXIDE

The general chemistry of titanium is complicated by the colloidal tendencies of some of the compounds of titanium under a variety of conditions. It is probable that this property has retarded the development of the chemistry of the element until more recent years. This tendency, which had been looked upon as unfavorable by chemists, has been mastered at least in part by industrial research men and is being used in the production of titanium pigments. The control of the formation of the colloidal hydrous titanium oxide and the conditions which exist during its subsequent coagulation are points which are regarded by industry as prime determining factors in the manufacture of titanium dioxide of the highest pigment quality. Much research along this line has been completed and investigations are being continued.

Titanium is unique in that it will appear in colloidal form in solutions containing large amounts of electrolytes. Systems have been prepared containing 60 grams of colloidal TiO_2 per liter in the presence of 400 grams per liter of sulfuric acid. This unique character of titanium is further emphasized by the fact that stable aqueous systems can be prepared containing more than 600 grams of colloidal TiO_2 per liter.[1] These systems are almost as fluid as water and can be prepared commercially at a cost not greatly exceeding that of pure TiO_2 pigment. The precipitated raw pigment is the most convenient starting material and the method of procedure consists simply in neutralizing the adsorbed sulfuric acid with alkali, washing the oxide until sulfate free, and treating the oxide slurry with about 2 grams of hydrochloric acid (conc.) for each 100 grams of TiO_2. The thick slurry or rather firm filter cake is transformed to a fluid liquid upon the addition of the hydrochloric acid. The process of peptization is readily reversed and coagulation occurs upon the addition of a small amount of sulfate or other polyvalent anions. The colloid is positively charged and all colloidal titanium systems known to the writers are positive when dispersed in an acid medium. In alkali media the charges may be reversed and negatively charged colloidal systems prepared.

ANALYSIS OF TITANIUM

Only a very brief summary of the analytical methods for titanium estimation will be given. For more details the reader is referred to Thornton's A. C. S. Monograph No. 33 on titanium.[2]

Titanium may be determined gravimetrically by hydrolysis of weakly acid solutions or by precipitation by special reagents, such as cupferron or tannic acid. It may be determined volumetrically by reduction of the salt by a suitable means, such as a Jones reductor, with subsequent oxidation with standard oxidizing agents. The element may be determined colorimetrically by means of the yellow color produced when H_2O_2 is added to an acid solution of a titanium salt. The resulting color is compared with similar solutions of a known titanium content.

These analyses cease to be simple when certain interfering elements are present. Gravimetric analyses, by methods which depend on hydrolysis of the quadrivalent titanium salts, give erroneous results because of the interference of aluminum, phosphoric acid, iron, chromium, etc. Cupferron is accepted as an excellent reagent for the precipitation of titanium but iron must first be removed. This is readily accomplished by making use of a special property of titanium, namely, that of remaining in alkaline solution in the presence of certain hydroxy organic acids such as citric and tartaric. Under these conditions the iron can be precipitated as the sulfide and removed by filtration. Upon adding acid and the cupferron reagent a precipitate is formed which can be ignited and weighed as TiO_2. Volumetric analysis is most commonly used because of the simplicity and speed of the operation. Standard ferric iron solutions are usually employed, for the presence of iron in the sample causes no interference. The endpoint is readily detected by the use of an alkali thiocyanate salt. The presence of certain impurities, which often occur in titanium ores, causes erroneous results. Vanadium is the worst offender. It is because of this interference that the gravimetric cupferron method is preferred.

COMMERCIAL USES OF TITANIUM AND ITS COMPOUNDS

A glance at the list of the uses of titanium (Table 2) shows that it is impossible to discuss all of them in detail.

TABLE 2

USES OF TITANIUM AND ITS COMPOUNDS

1. Titanium dioxide pigments
2. Titanium alloys
3. Ceramic industry
4. Dyeing industry
5. Leather industry
6. Analytical
7. Fertilizer
8. Smoke screens
9. Pyrotechnics
10. Therapeutics
11. Glass
12. Abrasives
13. Incandescent media
14. Titanate and tinted TiO_2 pigments

Iron-titanium alloys are by far the most important alloys of titanium. Several grades are on the market at present. They differ largely in their carbon content. The original ferrous-titanium alloy can be prepared by reduction of titaniferous ores with carbon,

[1] H. FREUNDLICH AND W. KROSS, "Titanium dioxide sols," *Kolloid-Z.*, **52**, 37–46 (1930).

[2] WM. M. THORNTON, JR., "Titanium, with special reference to the analysis of titaniferous substances," Reinhold Publishing Co. (successor to Chemical Catalog Co.), New York, 1927.

and may be prepared with various percentages of carbon. The alloy has been used for a very long time as a cleansing agent, added usually in the ladle. Titanium reacts with the N_2 and the O_2 and also refines the graphite flakes. Furthermore, the titanium carbide present in the alloy is soluble and forms a uniformly grained product. Used in this manner very little titanium remains in the steel. In fact, the alloys were such good cleansing agents that any other advantages to be gained from titanium were forgotten for a long time.

Lately these alloys have been used in the manufacture of gray iron (cast iron). They tend to close the grain of the thick sections, improve strength, and avoid hard spots or "chill" in thin sections. A cast gray-iron compressor cylinder has been exhibited in which the internal surfaces of the thick walls were dense and sound and the thin outer ribs and flanges were not chilled, cracked, or misrun. The low-carbon titanium alloys are used where it is desirable not to increase the carbon content of the product. These alloys may be produced by reduction with aluminum.

Titanium-aluminum alloy sold under the trade name "Webbite" is used to incorporate both of these elements in the final product. It increases tensile strength and produces a finer grain than when titanium is absent. The soundness of the castings is also improved.

The addition of titanium to copper produces an age-hardening effect similar to that of beryllium but is much cheaper. Copper-titanium alloys can be cast, and, if impurities other than titanium are absent, the electrical conductivity is not greatly impaired, providing the titanium content is low. The new nickel, molybdenum, and manganese titanium alloys also show great promise of becoming commercially important, especially since this age is becoming an alloy age.

TiO_2 has been used for a long time for the production of a honey-yellow underglaze on pottery and in the production of an ivory-white enamel for artificial teeth; a special grade of rutile sold under the trade name "Titanellow" is often used for the latter purpose. Titanium compounds have been used for coloring many clay products. It is gaining importance in the manufacture of acid-resistant enamels and refractory materials. The March 10, 1935, *News Edition* of *Industrial and Engineering Chemistry* describes a new corrosion-resistant rotary kiln. The synthetic silicate bricks used contain titanium, among other materials. TiO_2 is used in the production of enamels. When added to the usual enamel batch it tends to produce colored enamels, the color depending upon the other ingredients present and the amount of each. The colors produced vary from cream to tan and light blue to bluish gray. TiO_2 increases the fluidity of the vitreous enamel melt but is not an especially good opacifier. Vitreous enamels containing up to 14% TiO_2 produce stable white (and colored) acid-resisting enamels.[3]

The use of titanium compounds in the dye industry is old and rather well known. Their greatest use is as stripping agents for cotton, wool, and silk. A trivalent salt solution (usually sulfate) is used. It is also useful where goods have been misdyed, for many dyes can be removed by titanous salt; the cloth can then be washed, and immediately redyed. These solutions are also used for decolorizing old paper. TiO_2 has been used as a mordant but is not especially important in that rôle.

Titanium oxalate serves the double purpose, in the leather industry, of acting as mordant and of precipitating any free tannin that might throw down the dyestuff when vegetable-tanned leathers are dyed with basic coloring matters. When titanium is used with a striker logwood to produce black it does not cause the leather to become brittle. When used alone it gives a yellowish brown color suitable for shoe leather.

Titanous solutions are easily made, standardized, and stored. They are strong reducing agents and often used as such. Titanous solutions are used to detect copper in dyed goods. They produce the characteristic red colloidal copper color when that element is present. Titanium compounds are also used in detecting fluorine.

Titanium readily reacts with nitrogen and thus has been suggested as a possible source of fertilizer. Titanium fertilizers have not become commercially important.

Titanium tetrachloride is used to produce smoke screens. Those who attended the A. C. S. meeting in Washington in 1933 and who took the trip to Edgewood Arsenal may remember the smoke screen produced for us. We were informed that $TiCl_4$ was used.

Because of the brilliant white light produced titanium compounds have often been used in pyrotechnics.

A small amount of titanium compounds, especially sulfates and salicylates, is used in therapeutics.

Rutile has been used to produce glass, sometimes displacing SiO_2 altogether. Titanium compounds tend to make glass semi-opaque. The color of titanium-containing glass may be made blue or violet by employing a reducing atmosphere. Colorless glass containing titanium oxide is opaque to ultraviolet light and is important because of this property.

Titanium carbide is gaining in importance as an abrasive. It is cheaply made and very hard. It is often used in combination with other carbides, such as tungsten and molybdenum carbides.

A few years ago considerable interest was aroused in the use of titanium in the production of arc-lamp electrodes and of filaments. This interest seems to have subsided somewhat now, but may be revived because of the inherent possibilities of titanium in these materials.

TITANIUM DIOXIDE PIGMENTS

Titanium dioxide is by far the most important and useful compound of titanium. It is manufactured extensively for paint pigments and this industry has grown from its infancy in 1918 to become the producer of one of the major paint pigments. Until 1928 only the composite titanium pigments were marketed in any quantity. Since that time the pure TiO_2 has made

[3] DUTTON AND WAGNER, "Ti and Zr compounds—their application in enamels," *Ceram. Ind.*, **24**, 24–5 (1935).

rapid progress. The production of these pigments has been interestingly described in the literature.[4,5]

This pigment has the advantage of high hiding power, inertness, and great stability. The hiding power of a pigment is dependent on the particle size and the index of refraction. The former can be controlled by the method of manufacture, while the latter is constant for any specific crystal. Titanium dioxide has the highest refractive index of any known white crystalline material and should have the highest hiding power of any pigment. It has not yet been surpassed in this respect (see Table 3). Titanium dioxide pigment is being used to a very large extent in place of the older white pigments such as white lead, lithopone, zinc oxide, etc. It is the only pigment that can be used in certain of the new paints and enamels based on special synthetic vehicles. It is interesting to note that Prof. B. Smith Hopkins in his book on the rare elements refers to the cost of anatase in 1921 as $230 per pound. Today you can buy pure TiO_2 pigment (anatase) for about 18c. per pound.

TABLE 3

REFRACTIVE INDICES OF SOME WHITE PIGMENTS (WAIT AND WEBER)

Basic carbonate white lead	1.94–2.09
Basic sulfate white lead	1.93
Zinc oxide (ZnO)	2.02
Zinc sulfide (ZnS)	2.37
Titanium oxide (TiO_2)	2.52
Barytes ($BaSO_4$)	1.64
Calcium sulfate	1.59
Antimony oxide	2.09–2.29
Silica SiO_2 quartz	1.55

A new titanium pigment, lead titanate, was announced for sale to the public in 1935. It has a cream-yellow color and is said to be a good chalk retarder. The material is too new to justify any definite prediction as to its probable acceptance by the public.

Another new and interesting development is the production of tinted TiO_2 pigments. These pigments have been prepared in various shades of gray and buff. They are very resistant to fading and chalking. These materials are not as yet offered to the public but it may be stated that they are essentially pure TiO_2.

Table 4 shows that TiO_2 pigments are used in a large number of ways other than in the manufacture of paints, enamels, and lacquers.

TABLE 4

USES OF TITANIUM DIOXIDE PIGMENTS

1. Paints, enamels, lacquers	9. Soaps
2. Paper	10. Shoe polishes
3. Delustering rayon	11. Synthetic finishes
4. Linoleum	12. Leather finishes
5. Welding rods	13. Leather cloths
6. Rubber	14. Face powders
7. Printing ink	15. Catalysts
8. Plastic molding powders	

TiO_2 is added to whiten and to make the paper opaque even though thin. One application is to decrease the postage expenses on catalogs and magazines. Titanium papers are also especially suitable for waxing. It is stated that pie plates made of paper containing TiO_2 have been put through ovens of a Canadian bakery without excess loss of strength.[6] The titanium dioxide may be added either to the beater or to the formed sheet in the form of a coating. The volume of this business has grown rapidly in the last few years.

Early rayon had a great luster and this was the object of criticism from the ladies. It is now satisfactorily delustered by use of TiO_2, which is usually placed in the cellulose solution prior to the formation of the fibers.

Considerable TiO_2 is used in the production of the linoleum base as well as in the printing colors. It serves as an economical whitening agent by reason of its great opacity or hiding power.

TiO_2 is used in the production of welding rods to make more uniform welds. In combination with other substances, it acts as a very effective flux.

TiO_2, when added to rubber, gives the goods the maximum amount of whiteness per unit of dry pigment, thus enabling the properties of the rubber to be maintained in the highest degree.

Titanium pigments have two main uses in the printing-ink industry. In lithographing it is customary to print all colors on a white priming coat and not directly on the metal surface. TiO_2 is used to produce various tints with a minimum amount of solid material and to "bring out" especially strong colors.

White and colored casein plastics use TiO_2, as do many other plastics, to produce opaqueness and special colors. Molding powders use TiO_2 for the same purpose.

TiO_2 is used in soap flakes and white toilet soaps. It is added to prevent excessive transparency and to give solidity and whiteness to the finished products. Tooth pastes often contain TiO_2.

Shoe polishes, synthetic and leather finishes, and leather cloths use TiO_2 as the best opacifiers and best white pigment. Often it is the only pigment that can be used.

TiO_2 has almost completely replaced ZnO in face powders. It is non-poisonous and enables greater permanent whiteness to be retained with the smallest amount of pigment, thus retaining the useful properties of the other ingredients.

TiO_2 has been used for the production of catalysts but is relatively unimportant at the present time.

This outline indicates the importance of the titanium industries. About one hundred tons of TiO_2 pigments are being produced daily and the business involved amounts to millions of dollars a year. Surely the technical importance and the great abundance of the element merit greater consideration by the chemists of the world. We are looking forward to the time when all books on general chemistry will contain a chapter devoted exclusively to titanium.

[4] "The manufacture of titanium white," *The Industrial Chemist*, Nov., 1933, pp. 373–7.

[5] WAIT AND WEBER, "Titanium pigments," *J. Oil & Color Chemists Assn.*, **17**, 257–94 (1934).

[6] PAUL M. TYLER, "Titanium—its uses in metallurgy," *Metals & Alloys*, **6**, 93–6 (1935).

SOME CONTRIBUTIONS *of* CRYSTAL STRUCTURE RESEARCH *to* GENERAL CHEMISTRY TEACHING*

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THE MOLECULE

ONE OF the chief contributions of crystal structure research has been to correct and clarify the concept of the molecule. The existence of *small molecules*, usually conforming in atomic arrangement to chemists' previous conceptions, has been confirmed in many cases, especially among organic compounds. A few examples may be mentioned:

Solid iodine (*1*) consists of diatomic molecules. Rhombic sulfur (*2*) is composed of S_8 molecules, each molecule being a puckered ring. Arsenic "trioxide" (*3*) consists of molecules of the formula As_4O_6, each arsenic atom being bonded to three oxygen atoms and each oxygen to two arsenic atoms (Figure 1). The

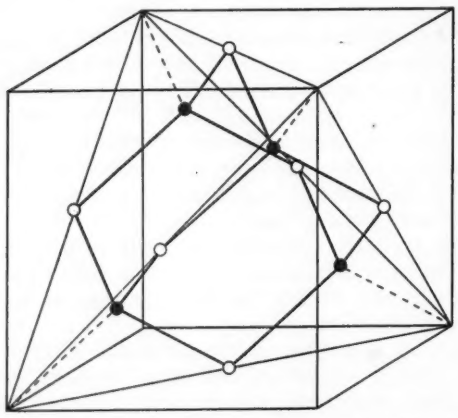

FIGURE 1.—ILLUSTRATING THE ARRANGEMENT OF ARSENIC ATOMS (DOTS) AND OXYGEN ATOMS (OPEN CIRCLES) IN AN As_4O_6 MOLECULE

Heavy lines indicate bonds between atoms; light lines and dotted lines are merely to aid in visualization.

mercurous halides (*4*) in the solid state are aggregates of Hg_2X_2 molecules, all four atoms being colinear: X-Hg-Hg-X. The paraffins and other "straight chain" compounds (*5*) consist of molecules in which the carbon atoms are in a zigzag arrangement. The benzene ring is a flat, regular hexagon (as a time average) in such compounds as hexachlorobenzene (*6*), C_6Cl_6, and hexamethylbenzene (*7*), $C_6(CH_3)_6$. The saturated cyclohexane ring, on the other hand, is puckered. In this and all other cases which have been studied in which a carbon atom is bonded by single bonds to four other atoms, the X-ray evidence favors the conclusion that these bonds are oriented approximately toward corners of a regular tetrahedron.

In some instances the crystal structure results have definitely decided between two or more alternative formulas. For example, the three nitrogen atoms in the N_3 group in azides (trinitrides) have been shown (*8*) to be in a linear arrangement rather than a ring.

Not only have the relative arrangements and distances within the molecules been determined for the compounds mentioned above and many others, but also the distances and relative positions of atoms in different (neighboring) molecules. Such information tells us much about interatomic and intermolecular forces and is proving increasingly useful in the development of theories of the dependence of melting points, boiling points, solubilities, and other properties on structure, in helping us to understand the mechanisms and rates of reactions, etc.

In this connection the writer wishes to emphasize the importance of pointing out frequently to students the dependence of the properties of substances on the *arrangements* of atoms as well as on their kinds and relative numbers. If the dependence of the formulas and structures of molecules and crystals on the structures of the atoms of which they are composed and the dependence of the uses of substances on their properties (as well as on various economic and social factors) are also stressed in the course, the students obtain an understanding of chemistry which is much more valuable than the accumulation of knowledge of unrelated (or slightly related) chemical facts.

Crystal structure results show that in many cases the molecule is as long as the crystal and sometimes also as broad and as thick. In the diamond (also silicon, germanium, and gray tin) the whole crystal is a single *giant molecule*, all of the atoms being linked together by typical non-polar electron-pair bonds (*9*). Another example is quartz, SiO_2, in which each silicon atom is bonded by single bonds to four oxygen atoms and each oxygen atom by single bonds to two silicon

* Presented before the Division of Chemical Education at the eighty-ninth meeting of the American Chemical Society, New York, April 26, 1935.

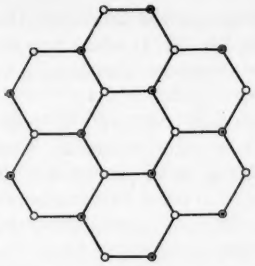

FIGURE 2.—A PORTION OF A LAYER MOLECULE OF ARSENIC, ANTIMONY, OR BISMUTH

Each atom is bonded to three others. Open circles represent atomic centers below the plane of the paper, dotted circles, those above the plane of the paper. The silicon layers in $CaSi_2$ are similar.

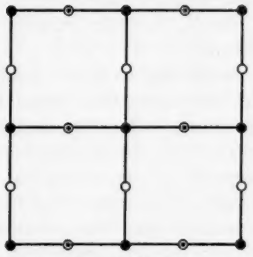

FIGURE 3.—A PORTION OF A LAYER MOLECULE OF HgI_2

Each mercury atom (large dot), in the plane of the paper, is tetrahedrally bonded to 4 iodine atoms, two of these being above (dotted circles) and two below (open circles) the plane of the paper.

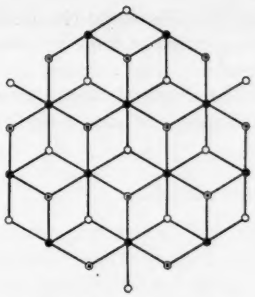

FIGURE 4.—A PORTION OF A LAYER MOLECULE OF $MgCl_2$

Each Mg atom, in the plane of the paper, is surrounded by six equidistant Cl atoms, three above (dotted circles) and three below (open circles) the plane of the paper. The $Mg(OH)_2$ structure is similar, with oxygen atoms replacing the chlorine atoms and with one hydrogen atom directly above or below each oxygen.

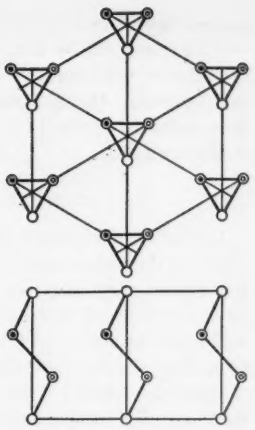

FIGURE 5.—HORIZONTAL AND VERTICAL PROJECTIONS OF A PORTION OF THE STRUCTURE OF SE (OR TE)

Each atom is bonded to two others in the same spiral chain.

atoms (*10*). (Incidentally, this structure and many others confirm G. N. Lewis' generalization that atoms other than C, N, O, and perhaps B rarely, if ever, form stable double or triple bonds. This explains the remarkable difference in properties between CO_2 and SiO_2, as well as many other otherwise anomalous differences between compounds of "first-row elements" and the corresponding compounds of "second-row elements.")

The elements phosphorus, arsenic, antimony, and bismuth have structures in which each molecule consists of a layer of atoms extending through the crystal (*9*). (See Figure 2.) *Layer molecules* likewise exist in mercuric iodide (*11*), magnesium chloride (*12*), magnesium hydroxide (*13*), and many other compounds (Figures 3 and 4).

In selenium (*14*), tellurium (*14*), cellulose (Figure 5) (*15*), rubber (*16*), proteins (*17*), and various other substances the molecules are long *strings* of atoms.

SALTS

Most salts in the solid state contain no small molecules. The salt crystal is either an assemblage of ions, as in sodium chloride and calcium sulfide (Figure 6), or is composed of giant molecules in which the bonds are polar (*i. e.*, the electron-pairs are shared unequally) and are easily broken to form ions. Mercuric chloride and magnesium chloride (Figures 3 and 4) are examples.

It is obvious that such crystals can go into or come out of solution one ion at a time. It is incorrect to consider the molecule in solution as a necessary or usual intermediate step in the precipitation or solution process.

IONS

Crystal structure research has definitely established the nature of water of hydration and water of crystallization (*18*). Around positive ions one frequently finds 4 or 6 or sometimes more H_2O groups, the oxygen atoms on the inside, the hydrogens outside. The ammonia

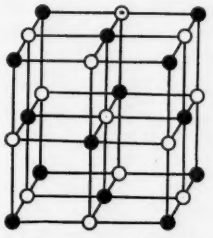

FIGURE 6.—REPRESENTING A PORTION OF THE NaCl STRUCTURE

Each atom is octahedrally surrounded by six equidistant atoms of the other kind. CaS has the same type of arrangement.

in the ammonia complexes is held by the positive ions in the same way as the water in the hydrated ions. The coördination number depends largely, but not entirely, on the relative sizes of the metal ion and the oxygen or nitrogen.

X-ray studies of crystal structures have shown conclusively that the nitrogen atom in substituted or unsubstituted ammonium salts is bonded to but four other atoms (*19*). The NH_4 or NR_4 group is tetrahedral and has a positive charge; this charge is, of course, balanced by a negative charge on some other atom or group of atoms.

Metal ions such as sodium and calcium have never been found to have as few as one or two oxygen neighbors in crystals. In $NaNO_3$ and $CaCO_3$, for instance, each Na^+ or Ca^{++} has 6 oxygen neighbors (*20*). It would seem justifiable to conclude that at ordinary temperatures such ions are always surrounded by oxygen atoms (or atoms of other electronegative elements) in the liquid state and in solutions as well as in crystals. Structural formulas indicating bonds connecting the metal atom to but one or two other atoms are not correct. If the metal atom is bonded at all to more negative atoms the bonds are more numerous and are quite polar.

Corresponding to the layer and string molecules mentioned above are *giant ions*. One simple example is the layer ion found in calcium silicide, $CaSi_2$. This substance is composed of layers containing only silicon atoms (*21*) arranged as are the arsenic atoms in the

arsenic layer molecule (Figure 2). The ionic charge is -1 for every silicon atom, this giving the same number of valence electrons as in arsenic. The calcium ions are between these layers. More complicated layer ions exist in mica (*22*). Asbestos contains complex string ions (*23*).

ATOMIC VALENCE SHELLS

Lewis' cubical atom theory (*24*) accounted beautifully for the valences of atoms and many other chemical facts and relationships. As early as 1916, however, Lewis concluded (*25*) (chiefly to account for double and triple bonds) that "at least in the case of the more nonpolar substances whose molecules are as a rule composed of atoms of small atomic volume" the valence shell usually consists of four pairs of electrons tetrahedrally arranged, rather than eight electrons at cube corners. A large amount of crystal structure evidence confirms this conclusion (*26*). *Electronegative atoms usually have tetrahedral valence shells.* To obtain such shells, 7-electron atoms such as chlorine, bromine, or iodine share one electron-pair with another atom; 6-electron atoms such as sulfur, selenium, and tellurium share two electron-pairs, giving rings or long strings; 5-electron atoms such as phosphorus, arsenic, etc., share three pairs; carbon, silicon, germanium, etc., share four pairs. In compounds, as well as in the elements themselves, the numbers and arrangements of the atoms are such as to give each negative atom a tetrahedral valence shell in most cases. Arsenic "trioxide," quartz, mercurous and mercuric iodide, magnesium chloride, and magnesium hydroxide may be cited as examples. There are hundreds more whose crystal structures have been determined.

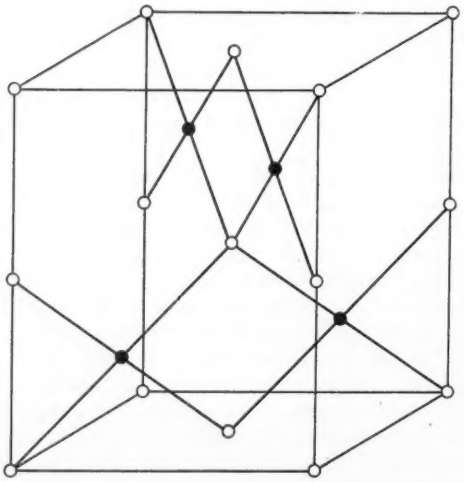

FIGURE 7.—A PORTION OF THE STRUCTURE OF PdO
Pd atoms are represented by dots, O atoms by open circles.

"Octahedral" valence shells, usually involving six bonds to neighboring atoms, are quite common among the more positive atoms and among the largest of the more negative atoms (*e. g.*, Sn, Sb, Te, I) when bonded to small, very electronegative atoms such as oxygen or fluorine.

According to some deductions by Pauling (*27*) from the new quantum mechanics, certain elements, such as nickel, palladium, and platinum in the divalent state and gold in the trivalent state, can form four stable coplanar bonds at corners of a square. Crystal structure results strikingly confirm this conclusion also. As examples may be mentioned the PdO structure (*28*) (Figure 7) and the structures of certain crystals (*29*) containing $PtCl_4^{--}$ and $AuCl_4^{-}$ ions.

PRIMARY AND SECONDARY VALENCE; VALENCE NUMBERS

Some years ago (*30*) the writer showed that by a simple extension of Lewis' valence theory one could account beautifully for the previously puzzling phenomenon of secondary valence. Since then a vast amount of crystal structure work has shown that the conception of secondary valence presented at that time was essentially correct. The situation may be briefly summarized as follows:

There is no difference between a primary valence *bond* and a secondary valence *bond*. One can, however, distinguish between primary valence *compounds* and secondary valence *compounds*. In the former the number of bonds around each atom equals its nonpolar valence number. In the latter this is not true. One can imagine a primary valence compound as being made from the uncharged atoms entirely by *primary valence reactions*, in which one electron of each shared pair comes from each of the two atoms sharing the pair:

$$A\cdot + \cdot B \rightarrow A : B$$

The formation of a secondary valence compound from neutral atoms involves (in addition) either electron transfers

$$A\cdot + \cdot B \rightarrow A^+ + :B^-$$

or *secondary valence reactions*, in which bonds are formed by the addition of a lone pair in the valence shell of one atom to the valence shell of the other atom:

$$A + :B \rightarrow A : B$$

As is well known, the organic chemists' valence numbers are not always identical with the valence numbers used in inorganic chemistry, *e. g.*, in balancing oxidation-reduction equations. The two types of valence number are related to the actual molecular and crystal structures in the following way (*28*).

The *non-polar valence number* of an atom equals the number of electron-pairs it shares with other atoms (*i. e.*, the number of bonds) plus the number of units of charge (+ or −) on the atom, considering one electron of each shared pair as belonging to each of the two atoms bonded together by that pair. The *polar valence number* of an atom equals the net charge on the atom, considering both electrons of each shared pair as belonging to the more electronegative atom.

These definitions conform to the valence numbers usually used. Any other non-equivalent definitions lead to different valence numbers.

Two examples may be cited: CH_2Cl_2 and the ammonium ion. In the former, the organic chemist gives carbon a valence of 4, corresponding to the 4 electron-pairs shared with other atoms. The inorganic chemist on the other hand gives carbon a valence of 0, since the assignment of all of the electrons shared between carbon and chlorine to chlorine and all of the electrons shared between carbon and hydrogen to carbon leaves a net charge of 0 on the carbon.

In the ammonium ion, NH_4^+ (and likewise in all ammonium salts), the nitrogen shares four pairs of electrons with other atoms, but since the net charge on the nitrogen atom is +1, if one electron of each shared pair is counted, the organic chemist gives nitrogen a valence number of 5. The inorganic chemist, however, assigns to nitrogen all of the electrons which are actually shared with hydrogen. This gives the nitrogen a net charge, and so a (polar) valence number, of −3.

IONIC EQUILIBRIA IN SOLUTION

Along with a better knowledge of the nature of secondary valence has come a better understanding of ionic equilibria in solution. Only a few examples will be considered here.

In any aqueous solution which, in the ordinary terminology, contains cupric ion and chloride ion, the equilibria represented by the following equations all exist:

$$Cu(H_2O)_4^{++} \rightleftarrows Cu(H_2O)_3Cl^+ \rightleftarrows Cu(H_2O)_2Cl_2 \rightleftarrows Cu(H_2O)Cl_3^- \rightleftarrows CuCl_4^{--}$$

The coördination number of copper, for both oxygen and chlorine neighbors, is assumed to be four; the four neighbors may be all chlorines or all oxygens (of H_2O groups) or intermediate combinations. The relative concentrations of the different ionic and molecular species present depend on the relative amounts of cupric copper and chlorine. Increasing the concentration of chloride ion shifts all of the equilibria to the right in accordance with the "equilibrium shift principle" (the Principle of Le Chatelier).

For simplicity or because in many cases the number of H_2O groups in the complex is unknown or uncertain, we may wish to leave these groups out of the formulas. The equilibria discussed in the preceding paragraph are then represented as follows:

$$Cu^{++} \underset{-Cl^-}{\overset{+Cl^-}{\rightleftarrows}} CuCl^+ \underset{-Cl^-}{\overset{+Cl^-}{\rightleftarrows}} CuCl_2 \underset{-Cl^-}{\overset{+Cl^-}{\rightleftarrows}} CuCl_3^- \underset{-Cl^-}{\overset{+Cl^-}{\rightleftarrows}} CuCl_4^{--}$$

Similar equilibria, between certain zinc ions and the zinc hydroxide molecule, may be represented in the following manner (assuming a coördination number of 4 for Zn surrounded by O):

$$Zn(H_2O)_4^{++} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Zn(H_2O)_3OH^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Zn(H_2O)_2(OH)_2 \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Zn(H_2O)(OH)_3^- \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} Zn(OH)_4^{--}$$

Omitting the H_2O groups these become:

$$Zn^{++} \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}} ZnOH^+ \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}} Zn(OH)_2 \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}} Zn(OH)_3^- \underset{-OH^-}{\overset{+OH^-}{\rightleftarrows}} Zn(OH)_4^{--}$$

The equilibria are shifted by changing the acidity and basicity of the solution. The shifts in this case involve not the *replacement* of H_2O by OH^- or vice versa but merely the removal or addition of a hydrogen ion (*i. e.*, a proton). The hydrolysis of zinc ion is nothing more than the loss of one or two protons from the H_2O groups around the zinc. Uncharged zinc hydroxide molecules can either add or lose protons; this is an alternative way of saying that zinc hydroxide is amphoteric. If the concentration of zinc hydroxide molecules becomes sufficiently great, solid zinc hydroxide, $ZnO \cdot xH_2O$ (containing an indefinite amount of water, depending on temperature and other factors), is precipitated.

The above-mentioned equilibria between zinc ions and the zinc hydroxide molecule are quite analogous to the following:*

$$\begin{array}{lll} HClO_4 \rightleftarrows ClO_4^- & & \\ \text{or} & & \\ Cl(OH)O_3 & & \\ H_2SO_4 \rightleftarrows HSO_4^- \rightleftarrows SO_4^{--} & & \\ \text{or} \quad \text{or} & & \\ S(OH)_2O_2 \quad S(OH)O_3^- & & \\ H_3PO_4 \rightleftarrows H_2PO_4^- \rightleftarrows HPO_4^{--} \rightleftarrows PO_4^{---} & & \\ \text{or} \quad \text{or} \quad \text{or} & & \\ P(OH)_3O \quad P(OH_2)O_2^- \quad P(OH)O_3^{--} & & \end{array}$$

The ability of an XO_4 group to hold hydrogen ions depends primarily on the kernel charge of the central atom X. X atoms which are somewhat "larger" than those considered above have a larger coördination number for oxygen, usually six. Equilibria such as those listed below then exist.

$$\begin{array}{l} Al(H_2O)_6^{+++} \rightleftarrows Al(H_2O)_5(OH)^{++} \rightleftarrows Al(H_2O)_4(OH)_2^+ \rightleftarrows \\ \qquad Al(H_2O)_3(OH)_3 \rightleftarrows Al(H_2O)_2(OH)_4^- \rightleftarrows \\ \qquad Al(H_2O)(OH)_5^{--} \rightleftarrows Al(OH)_6^{---} \end{array}$$

$$\begin{array}{lll} Sn(H_2O)_6^{+4} \rightleftarrows Sn(H_2O)_5(OH)^{+3} \rightleftarrows Sn(H_2O)_4(OH)_2^{+2} \rightleftarrows & & \\ \text{or} \quad \text{or} \quad \text{or} & & \\ H_{12}SnO_6^{+4} \quad H_{11}SnO_6^{+3} \quad H_{10}SnO_6^{++} & & \\ Sn(H_2O)_3(OH)_3^+ \rightleftarrows Sn(H_2O)_2(OH)_4 \rightleftarrows & & \\ \text{or} \quad \text{or} & & \\ H_9SnO_6^+ \quad H_8SnO_6 & & \\ Sn(H_2O)(OH)_5^- \rightleftarrows Sn(OH)_6^{--} \rightleftarrows & & \\ \text{or} \quad \text{or} & & \\ H_7SnO_6^- \quad H_6SnO_6^{--} & & \\ Sn(OH)_6O^{-2} \rightleftarrows, \text{ etc.}, & & \\ \text{or} & & \\ H_8SnO_6^{-2} & & \end{array}$$

* Here and in the next group of equations "$-H^+$" and "$+H^+$" above and below each double arrow are omitted for simplicity.

$$I(OH)_5O \rightleftarrows \underset{\text{or } H_5IO_6}{I(OH)_4O_2^-} \rightleftarrows \underset{\text{or } H_3IO_6^{--}}{I(OH)_3O_3^{--}} \rightleftarrows$$

$$\underset{\text{or } H_2IO_6^{-3}}{I(OH)_2O_4^{-3}} \rightleftarrows \underset{\text{or } HIO_6^{-4}}{I(OH)O_5^{-4}} \rightleftarrows IO_6^{-5}$$

HYDROGEN BRIDGES

Considerable evidence, largely from crystal structure investigations, has accumulated for the existence of "hydrogen bridges" or "hydrogen bonds" between electronegative atoms (*31*). In the hydrofluoride ion, HF_2^-, the hydrogen, as a time average at least, is midway between two fluorine atoms (*32*): $\left(:\ddot{F}:H:\ddot{F}:\right)^-$. In ice (*33*), sodium hydrocarbonate (*34*), sodium dihydrophosphate (*35*), and certain silicates the X-ray results show similar hydrogen bridges between two oxygen atoms.

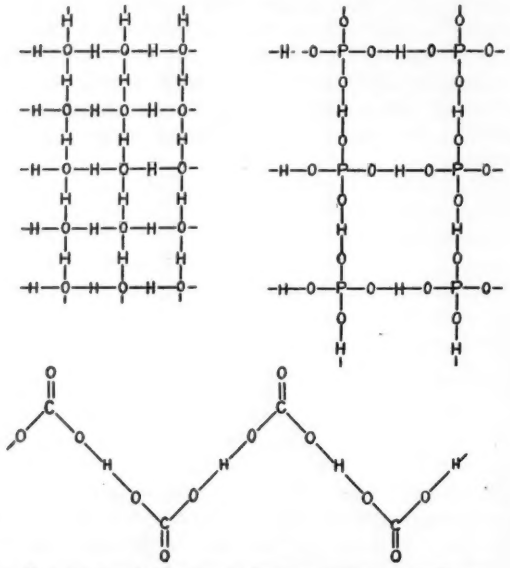

FIGURE 8.—A SCHEMATIC REPRESENTATION OF HYDROGEN BRIDGES CONNECTING "H_2O MOLECULES" IN ICE, "$H_2PO_4^-$ IONS" IN KH_2PO_4, AND "HCO_3^- IONS" IN $NaHCO_3$

(See Figure 8.) It is probable that the "heads" of fatty acid molecules in the solid state are usually joined together by such hydrogen bonds, and recent X-ray results obtained in this laboratory seem to be best explained by the assumption of structures of this type in liquid water.

SOLUBILITY

From a knowledge of its structure the "lattice energy" of a solid salt, *i. e.*, the energy change involved in the (hypothetical) expansion of the crystal until all of the component ions are separated by large distances, can be calculated (*36*). The difference between the lattice energy and the sum of the "hydration energies" or "solution energies" of the ions (the change in energy when they dissolve in water) is the energy of solution of the solid salt in water. This is nearly identical with the heat of solution of the salt. The free energy change on solution, which is proportional to the logarithm of the solubility product, is the difference between the heat of solution and the product of the entropy change and the absolute temperature:

$$\Delta F = \Delta H - T\Delta S$$

Since the entropies of solution are available (*37*), a satisfactory quantitative treatment of solubilities is now possible, at least for simple salts.

"LAWS"

Crystal structure investigations have furnished much information regarding the existence and nature of solid solutions. In the solid state as in the liquid and gaseous states solutions are not rare, in spite of the neglect of the subject of solid solution in most general chemistry courses. There is no sharp boundary line between a solution and a "pure compound" except an arbitrary one of definition. The "law" of definite proportions is not a law but a definition of a "pure compound."

A somewhat similar state of affairs exists with regard to the "law" of simple multiple proportions. This "law" is only true if we refuse to consider intermetallic compounds, organic compounds, many compounds of Si, Mo, W, Ta, etc.

CONCLUSION

The examples which have been given, although by no means exhaustive, serve to show in how many ways the results of crystal structure analysis affect the teaching of a course in general chemistry. As research in this field continues, many further and equally important contributions are to be expected. An increase in our knowledge and understanding of the structure and behavior of matter must be followed by corresponding changes in the subject matter of our fundamental courses and even in teaching methods.

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FLAME-SPEED DEMONSTRATIONS

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FLAME-propagation demonstrations for first-year classes in chemistry can be conveniently performed with simple apparatus. Three lengths (15 ft.) of glass tubing of 2-cm. bore are laid end-to-end on the table and connected with tape. A Meker burner having an outlet of about the same diameter as the glass tubing is used to give the gas-air mixtures.

In order to get a flame of about maximum speed the gas supply is adjusted with the air-port wide open until the flame is judged to be at maximum efficiency. The flame is then pinched off with a clamp or by kinking the rubber tubing, and then the burner with the gas-air mixture flowing through it is held against one end of the glass tube for about 30 seconds. This end of the tube is then closed with a stopper. The assistant ignites the mixture and with a stopwatch takes the time for the flame to travel the length of the tube.

The time for a rich mixture is taken in the same way except that the air-port of the burner has been closed about halfway. For a lean mixture the air-port is wide open but the gas supply is cut down so that the flame begins to flicker. More time will be required to displace the air from the tube. That there is a partial vacuum behind the flame due to the condensation of the water formed may be shown by inserting a stopper holding a bent tube into the end of the ignition tube after ignition of the mixture and allowing water to be sucked up through the bent tube.

When both ends of the tube are left open the flame surges and its velocity is accelerated, especially for the last third of its course. Other variations suggest themselves to the teacher. A circle of wire gauze inserted at one of the joints will stop the progress of the flame, thus demonstrating the principle of the miner's safety lamp. If the air-port is allowed to draw in oxygen instead of air it can be shown that the flame speed is increased. When ethylene is used a lean mixture will give a luminous, peculiarly shaped, fuzzy-appearing flame. For natural gas which had been enriched the following results were obtained: maximum, 6.8 secs.; rich, 13.6 secs.; lean, 13.6 secs. For ethylene the following results were obtained: maximum, 7 secs.; rich, 14.6 secs.; lean, 22 secs.

With these demonstrations the teacher can show that the theoretically required amount of air or oxygen furnishes a combustible mixture in which the maximum flame speed is attained, and that the flame speed depends upon the kind of gas being burned. He can call attention to the fact that the burner has here a function similar to that of the carburetor. He can explain why violent gas explosions sometimes occur in the kitchen gas oven when the flame has been turned too low and goes out and an attempt to relight it is made without proper ventilation. Students observe these demonstrations with great interest and generally learn the principles involved.

The DEMONSTRATION METHOD *of* TEACHING CHEMISTRY*

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THERE is evidence that in Alexandria, under the Ptolemies in the third century before Christ, there existed a state-supported institution in which students of man and of nature could come into personal contact with the objects of study, and by the aid of such appliances as were then available could carry on scientific investigations. The practical study of anatomy, physiology, pathology, and other natural sciences was here cultivated. This school was gradually converted into an organization for metaphysical discussions.[1]

Fifteen hundred years elapsed before a trace of any practical work in science is found. In 1231, Frederick the Second commanded the teachers at Salernum to cultivate the study of anatomy. After the passage of this edict, occasional dissections of the human body were made, but little of practical value was accomplished for two centuries. In the latter half of the fifteenth century an active interest was developed in the study of the human anatomy, which resulted in the famous work of Versalius published in 1543.[2]

The first scientific laboratory for purposes of research, as well as instruction, was the anatomical laboratory.[3] For over 600 years there has been at least some practical instruction in anatomy; for over 300 years there have existed anatomical laboratories for purposes of teaching and investigation.

Doubtless Aristotle had his laboratory, and there might have been many private laboratories; but we are interested primarily in those for instructional purposes. It is certain that physical or natural science laboratories were not open to students until after the first quarter of the nineteenth century. This was partly due, no doubt, to the lack of proper facilities. Amos Comenius, the famous Moravian writer on education, advocated in 1657 the use of object lessons in teaching. He is quoted as saying, "Who is there who teaches physics by observation and experiment instead of by reading an Aristotelian or other textbook?"[4]

Methodical experimentation in the sciences of nature was definitely established by Galileo, and was zealously practiced by his contemporaries and successors in the seventeenth century. This movement was greatly promoted by the foundation of learned societies, such as the *Accademia dei Lincei* and the *Accademia del Cimento* in Italy, the *Collegium Curiosum* in Germany, the *Académie des Sciences* in Paris, and the Royal Society in England. It was at this time that a considerable portion of the classical apparatus employed in physical experiments was invented. In the eighteenth century there existed cabinets of physical apparatus to be used in demonstrative lectures, but they were inadequate, and suitable rooms for experimental work scarcely existed.[5]

It was not until the middle of the nineteenth century that any trace of the beginnings of a modern laboratory is found. Lord Kelvin, then Wm. Thomson, about 1845 established a physical laboratory at the University of Glasgow in an old wine cellar of a house. Wiley quotes him as saying, "This with the bins swept away and a water supply and sink added, served as a physical laboratory for many years."[6] As late as 1863, Magnus opened in Berlin his laboratory for experimental physical research. It was not, however, primarily for instructional purposes, and laboratory work was regarded as an institution for the privileged few.

In 1830, thirty years after the death of Lavoisier, the first chemical laboratory in the modern sense was established by Liebig in the University in Giessen. In this laboratory, students were given courses in qualitative and quantitative analysis. It was primarily due to the influence of these German universities that the laboratory form of instruction attained such popularity and grew so rapidly.[7]

About the same time, or shortly after the establishment of Liebig's chemistry laboratory, the academy was the prevailing secondary school, and it was for the first time in these schools that laboratories were established for students in secondary grades. Bowers found that 16 academies in North Carolina, 5 in Massachusetts, 4 in Connecticut, and 10 in New York offered chemistry, and some of these in their announcements set forth the claim that they had apparatus to illustrate the lessons in philosophy and chemistry.[8]

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The first record of laboratories in public schools is found in the history of Central High School of Philadelphia; the building erected in 1854 had provision for a chemistry laboratory. About the same time, as related by Wells, a laboratory was installed in the first high-school building erected in Chicago.[9] According to Tice, the first high-school building in St. Louis was provided with a laboratory for instruction in chemistry.[10] Downing claims that this form of instruction was not in practice until about 1890.[11] However, Harvard University took the lead in making laboratory instruction a college entrance requirement in 1886, and surely there must have existed a few public laboratories before that date. This makes the institution approximately fifty or sixty years old.

The establishment of laboratories enjoyed a natural growth for the next ten years (1890–1900). In the literature of 1900 to 1910, many articles condemning this type of work may be found, and not until 1910 to 1915 were educators willing to give the laboratories an opportunity to show what they could accomplish. Since 1915, the educational values of laboratory work have been lauded, and described by nearly all authorities as the one and only means of science instruction.

In order to approach the problem we are dealing with intelligently, it is necessary to discover the psychological processes involved in learning which justify or condemn the employment of a laboratory for instructional purposes. Evidently it is the product unobtainable without the laboratory which gives this practice its justification. Only after the real worth of the method established had been questioned was it thought necessary to justify its existence, and then it was that a flood of justifications overwhelmed adverse criticism. An early writer said:

> The educational value of the laboratory cannot well be overestimated. The student learns that to really know things, it is necessary to come into direct contact with things, and that this knowledge only is real and living, and not that which comes from mere observation of external appearances, or from reading or being told about them or still less from merely thinking about them.[12]

Herbert Spencer, in his chapter on "What knowledge is of most worth," attempts to show that the information which the study of science furnishes is incomparably more useful for our guidance in life than any other kind, that is, starting from the thesis that education is intended to teach us how to live. He states:

> That for discipline, as well as for guidance, science is of chiefest value. In all its effects, learning the meaning of things is better than learning the meaning of words. Whether for intellectual, moral, or religious training, the study of surrounding phenomena is immensely superior to the study of grammars and lexicons.[13]

He further contends that history and languages change, but the knowledge that chlorine is a disinfectant is a truth that will bear on human conduct ten thousand years hence.[14]

In a book dealing with the teaching of physics and chemistry written in 1902 by Alexander Smith, of The University of Chicago, and Edwin H. Hall, of Harvard University, the following statement is presented in support of the laboratory method.

> The employment of the laboratory method in Science furnishes an exercise not merely for the senses but for the mind.[15]

Harvey quotes President Eliot as saying:

> The student of natural science scrutinizes, touches, weighs, measures, analyzes, dissects, and watches things. By these exercises his powers of observation and judgment are trained, and he acquires the precious habit of observing the appearances, transformations, and processes of nature.[16]

Among later writers we find many similar dogmatic statements regarding the benefits assigned to laboratory instruction. Newell says:

> Demonstrations please a majority; informal conferences help a minority; examinations irritate a plurality; textbooks are studied and believed, but the real mental work begins when the student enters the laboratory.[17]

He further states that demonstrations thrust both problems and their solutions upon the student, and that a good instructor guides the student out of wrong or dangerous paths in a well-regulated laboratory.

A laboratory is defined by Harvey as a place in which difficulties may be isolated and attacked one at a time. He adds that it is a place in which phenomena can be controlled, and by the variation of a single factor, the effect of each may be described. The isolation of a difficulty he describes as similar to the process of abstraction in formal logic, and as one essential requisite for all successful study and for all good teaching. For example, he says:

> It is impossible to discover how far a body will fall freely in one second, unless there are means for describing the beginning and end of one second accurately, and designating the time at which the body shall begin to fall and when it shall stop. This process embodies the psychological principle of abstraction, the finer discriminations, and the developing of clear ideas that facilitate thinking.[18]

Thinking he defines as the perception of relations; that all our knowledge may be reduced to two forms, knowl-

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[17] NEWELL, L. D,, "Profit and loss in experimental chemistry," *Sch. Sci. Math.*, **7**, 165–75 (1907).

[18] HARVEY, N. A., "Psychology of laboratory science," Reference 12, p. 538.

edge of facts and knowledge of relations between facts. He cites the experiment of Buckingham who showed that in history there is a positive correlation between remembering and thinking; that is, a pupil who surpasses another by 1 point in the ability to remember, or accumulate facts, surpasses the other by .89 of a point in thinking. Harvey further justifies the laboratory form of instruction by saying that it furnishes ideas that are unusually vivid and clear, for in the laboratory work the several sensations which constitute the ideas derived from the study of books, or from lectures heard, are accompanied by only weaker, centrally initiated impulses. As a result of this statement, his contention is, therefore, that a laboratory furnishes ideas more clearly and vividly, and consequently relations between ideas are more readily discovered and more easily accomplished.[18]

Goddard maintains that the purpose of the laboratory is to give adequate experience and objective illustration from an understanding and appreciation of a science, and to give an understanding of the application of these to common processes and phenomena.[19] Many writers claim that the laboratory is the logical breeding place for a scientific attitude and justify its existence on this ground alone. Bowers expresses a similar attitude toward this problem by saying:

> Laboratory work is necessary to scientific thinking for the reason that in most laboratory exercises, the story is not told nor the problem solved, as long as the worker deals with spectacular observation, or gross facts. Laboratory work leads the worker on to scientific observation and to a breaking up of facts into simpler elements. It is data received from actual laboratory work that impel the student to think constructively, to make recombinations of mental processes, and to combine ideas that have never been combined before. The presence of the material apparatus makes a more vivid mental picture which aids in imagining the processes.[20]

Most writers upon this problem contend that the following values are to be derived from the laboratory form of instruction: (1) development of ingenuity, (2) development of scientific reasoning, and (3) provision for individual freedom.[21]

The development of the students' efficiency as a result of the collection and possession of knowledge derived from the laboratory exercises, is one of the chief advantages of the laboratory form of instruction, according to Gordon.[22] This belief is illustrated by Bowers, who contends that the saving of specimens by the shallow, undeveloped student may be the greatest incentive for the development of care and accuracy.[20] That the laboratory method of instruction preserves the interest of the class to a greater extent than the demonstration method is suggested by the following quotation:

> The laboratory work cultivates an interest in Science as the stage does in literature, but those taking part in the play are getting greater educational values from the work than are the audience which are the students.[20]

According to Downing, a laboratory provides freedom for the student in the collection of his own data, the tabulation of the facts he has discovered, the statement of his own hypotheses and their proving, and the formulation of his conclusions. These activities, according to this writer, develop habits of scientific thinking and self-reliance in the formation of opinions.[23]

In the preceding paragraphs an attempt has been made to treat briefly the development of the laboratory method and to present some of the claims made regarding its value. The writer will now endeavor to present a brief review of some typical investigations containing experimental data with regard to the relative value of the laboratory and demonstration forms of high-school science instruction.

The investigations will be described in chronological order, the first having been conducted by Cunningham in 1920.[24] In evaluating the demonstration and the laboratory methods of teaching botany, he selected those experiments suitable for both demonstration and individual laboratory work. Two classes were given Chicago Intelligence Tests and were equalized by selecting ten students out of each class for control groups. On one day Cunningham performed a demonstration before a certain group, and on the succeeding day permitted the students to perform individual experiments in the laboratory. The demonstrations were conducted according to the same mimeographed sheets that were given as directions for laboratory procedure. In measuring results, Cunningham employed two types of tests, one for the purpose of measuring temporary knowledge gained, and the other to measure knowledge permanently retained. The first test was given immediately after the completion of the laboratory or demonstration performance, and the other test was given several weeks after each experiment. His results in both types of tests showed superiority for the demonstration method.

In 1922, Cooprider made a report on a similar investigation in biology.[25] He divided a class of 68 students into 4 groups of equal ability as determined by mental ability examinations. Each of the four groups was given four different methods in instruction described by the author as follows:

1. Demonstration with oral instructions.
2. Demonstration with written instructions.
3. Individual work with oral instructions.
4. Individual work with written instructions.

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[19] GODDARD, H. N., "Laboratory teaching," *Sch. Sci. Math.*, **16**, 710–9 (1916).

[20] BOWERS, W. G., "Some educational values in the laboratory," *Education*, **44**, 546–55 (1924).

[21] MATHEWS, I. J., "Some present laboratory methods indicated," *Sch. Sci. Math.*, **16**, 767–8 (1916).

[22] GORDON, N. E., "Application of educational psychology to chemical education," *ibid.*, **21**, 862–7 (1921).

[23] DOWNING, E. R., "The relative value of laboratory instruction," *Sch. & Soc.*, **19**, 769 (1924).

[24] CUNNINGHAM, H., "The relative value of the lecture-demonstration and laboratory methods of instruction." Master's thesis on file in the Dept. of Natural Science, University of Chicago.

[25] COOPRIDER, J. L., "Laboratory method in high-school science," *Sch. Sci. Math.*, **23**, 523 (1923).

Twelve experiments were used, which means that each group was given three experiments in each of the four methods employed. Comparisons were made from the results of tests given immediately after each experiment, and tests given one month later. From the first set of tests Cooprider arrived at the following conclusions:

1. Oral instruction gives better results than written instruction.
2. Demonstration work is more effective than individual work.

From the results of the tests given one month following each experiment, he drew the following conclusions:

1. Demonstration work gives better results with oral instructions.
2. Laboratory work gives better results with written instructions.
3. Laboratory instruction is superior to the demonstration method.

A possible criticism is that the groups involved in this experiment were too small for the discovery of the proper instructional procedure and that rotating the method with every three experiments prevented a valid comparison of the data obtained, because of the two-fold variation in procedure and lesson content. In addition, those pupils taught by the demonstration method at the beginning of the investigation might have made greater progress later in their individual laboratory work as a result of having observed the expert performance of laboratory exercises.

Another experimental investigation was conducted by Kiebler and Woody[26] in the Hillsdale High School, Michigan. The purpose of this study as stated by the writers was "to evaluate the merits of the individual laboratory method and the demonstration method of teaching physics." In describing the methods employed in their investigation, the writers stated that the same textbook assignments, the same references, the same discussions preceding and following each experiment, and the same write-ups were made, the main difference between the two methods being that the laboratory groups performed the experiments from the directions given in the manual, while the demonstration groups developed a method of procedure in class without a laboratory manual and observed the performance of the experiments by the instructor and one or two student assistants. Fourteen experiments in "heat" were undertaken in this study by two groups of students, equated on the basis of scores made on the Army Alpha Test. With the first seven experiments the individual laboratory method was employed with one group and the demonstration method with the other, and with the last seven experiments the methods were reversed in order that each group might be exposed to the two different forms of instruction.

The investigators stated that three different types of tests were administered in an attempt to measure the effectiveness of the two methods. They were listed as follows:

1. Tests for temporary or immediate knowledge of the facts of the experiments.
2. Tests for permanent or delayed knowledge.
3. A test for knowledge of how to apply the principles and technic learned in attacking a new problem.

A test of the first type was given from one to two weeks after each experiment; the second-type test was administered two weeks after the completion of the seven experiments; and the third-type test, according to the report, was a new problem: "To find the temperature of a white-hot body." In describing this test the writers stated:

> Pupils were furnished with a list of the apparatus needed for the experiment and were then given an informal test in which they were asked to make a simple drawing showing how the apparatus would be used and to fill out broken sentences describing a possible method of procedure. Each student in the individual laboratory group then performed the experiment, while in the other group the instructor gave a demonstration. Two weeks later both groups were rigorously tested again.

In the construction of the tests an attempt was made to produce tests as objective as possible by using the types of questions usually found in standardized tests, such as "completion," "matching," etc.

Kiebler and Woody stated that on the basis of the data obtained from the scores made on these tests, the following observations seem justified.

1. The results secured through the use of the demonstration method were as good, if not superior, in all three types of tests given—the test for immediate knowledge, for permanent knowledge, and for knowledge of how to apply principles and technic in solving a new problem; while the advantage in favor of the demonstration method was small, it was very significant.
2. The individual method tended to be superior in those experiments that are especially difficult to perform or in which great care must be exercised to see the exact procedure. Such facts suggest that the most effective method depends upon the nature of the experiments themselves and suggests the need for scientifically classifying them.
3. When the demonstration method gives equal or superior results, it is to be preferred to the individual laboratory method, because it saves about one-half of the time usually devoted to performing the experiments and permits the instructor to use the time thus saved in relating the facts and principles to allied phenomena. Furthermore, the enthusiasm of the class working together is most valuable.
4. New problems involving principles and technic already learned arouse much interest and enthusiasm and offer opportunity for rich returns in teaching.
5. The results of the experiment suggest that in the smaller high schools, at least, better teaching would result, and much money would be saved if the laboratories could be arranged and equipped so as to facilitate demonstration of many of the experiments instead of trying to provide apparatus for the individual performance of all of them.

Anibal[27] reports a study entitled, "Investigation of

[26] KIEBLER AND WOODY, "The demonstration versus the laboratory method for teaching high-school physics," *J. Educ. Research*, **7**, 50–9 (1923).

[27] ANIBAL, A. G., "Investigation of demonstration versus laboratory as a method of teaching natural science," *Proc. Nat. Educ. Assoc.*, **62**, 771–3 (1924).

Demonstration versus Laboratory as a Method of Teaching Natural Science." An abstract of this report, as presented by the investigator, is as follows:

Desiring to show by purely objective methods whether adequate instruction could be given by the lecture method as efficiently if not better than by the laboratory method, an experiment was made in the regular chemistry classes of Central High School, Kansas City, Missouri.

Two classes were first balanced by shifting students from one to the other, after the ability of each student had been determined by the use of general intelligence tests. The groups were then taught, one by the regular procedure of individual laboratory work and the other by the method of lecture demonstration. The experiments were demonstrated before the class without the students having any contact whatever with the apparatus or the materials. At frequent intervals both groups were tested by means of the same objective tests, and the results compared.

The lecture-demonstration method consistently gave better results all the way through the experimental study. The students seemed to understand the fundamental principles of chemistry better. Perhaps this is due to their being less distracted by the novelty and also complication of the apparatus, than when they have to set up the equipment and try the experiment also, as in the case of the individual laboratory method of instruction.

The results of the first investigation were checked by a similar experiment made with two similarly balanced groups of high-school students after the completion of the first study. The second investigation confirmed the results arrived at in the first study.

The cost of the lecture-demonstration method is remarkably lower. Only one complete supply of equipment is required in this method, as contrasted with the cost of about fifteen complete sets in use when the students do the work by individual laboratory procedure. Much building space is also saved in that the lecture-demonstration room need not be more than one-third the size and space ordinarily given over to the regular chemistry laboratory. The cost of the laboratory furniture required to do the work by lecture-demonstration would not be one-tenth the amount that is necessary to meet the requirement for the individual laboratory method of instruction.

From the preceding discussions of various investigations concerning the relative value of the laboratory and the demonstration forms of instruction, it will be noted that the majority of the experimental data show a superiority for the demonstration method. Laird[28] says, "The bulk of opinion is pro-laboratory, the most reliable experimental data is con-laboratory."

The students' attitude toward their work is an important problem, in the judgment of Laird; some of the students in the laboratory courses in psychology, with which Laird was concerned, possessed attitudes of mild antipathy and others of even positive dishonesty in the performance of the experiments.

In 1927 the writer reported an investigation on the relative merits of the demonstration method as opposed to the laboratory method of teaching high-school chemistry.[29] An abstract of this experiment as presented by the investigator is as follows:

Problem—To determine the relative value of the individual laboratory versus the demonstration method of teaching high-school chemistry.

Method—Four regular chemistry classes in the Austin, Texas, High School were made equivalent in mental ability on the basis of scores made on the Miller Mental Ability Test. One class was taught by the demonstration method and another by the individual laboratory method by each of two instructors, who observed great care to have all conditions and factors identical with their respective pairs of experiment and control groups, except the competing methods. Ten laboratory exercises in chemistry were performed by pupils and by teachers according to procedures outlined in a standard laboratory manual. On the day following each experiment a test for immediate retention was administered. Three weeks after the ten experiments had been performed a test for delayed retention was administered. On the day following the completion of the exercise, a third test was given, consisting of a laboratory problem with which the pupils had not been previously confronted. This test was intended to measure a laboratory method of attack, not apparatus manipulation.

Findings—The experimenter is convinced that the demonstration method is superior to the individual laboratory method, both for immediate and delayed retention; and that it is superior in providing the "average superior pupil" with a knowledge of technic for attacking new problems, though slightly inferior in this respect for the "average inferior pupil." He further believes that the demonstration method is superior in providing opportunity for adapting the laboratory work to individual differences in mental ability.

In 1928, Horton[30] reported his findings in regard to the relative values of teacher demonstration and individual work in the laboratory. This experiment was conducted over a period of two years in the Seward Park High School, New York City. The experimenter first analyzed fifteen widely used chemistry manuals to determine the manipulative skills and technics involved in laboratory exercises. Thirty-five of the one hundred eight simple technics thus found were judged by a group of competent authorities in the field of chemistry education to be desirable habits and eighty-six to be of such importance that they should be included in the course either as habits or models. The experimenter conducted his investigation with equivalent groups, taught respectively by the demonstration and the individual methods. Results were tested with both written tests and non-written tests designed to measure objectively the laboratory skills and abilities previously determined. He also attempted to evaluate the problem method of laboratory instruction. His findings, reported in abstract form, are as follows:

Findings—Results with the written tests seemed to show some functioning of laboratory work in assisting pupils to succeed in written tests, but the experimenter believes that the results indicate that written tests are ill-adapted to indicate or measure what may nevertheless be learned in the laboratory. The results with the non-written tests seemed to show a significant superiority of the individual method over the demonstration method for purposes of performance.

The results with the written tests show no significant superiority of either the individual or the demonstration method for training to succeed in written tests. The experimenter believes, however, that written tests of the kind in prevailing use are not capable of detecting differences in the outcomes of laboratory

[28] LAIRD, D. A., "Report on students' attitude toward laboratory courses," *Sch. & Soc.*, **19**, 589–92 (1924).

[29] KNOX, W. W., "The demonstration method versus the laboratory method of teaching high-school chemistry," *Sch. Rev.*, **35**, 376–86 (May, 1927).

[30] HORTON, R. E., "Some measurable outcomes of individual laboratory work in chemistry," The Department of Superintendence, Sixth Yearbook, p. 351.

methods. The results with the non-written tests seemed to show that the "problem method" is superior to the individual and the demonstration methods. The experimenter concludes that if ability to do experimentation or to solve perplexities of a chemical nature are desirable goals, practice in this experimentation, not practice in watching somebody else experiment, is necessary. He concludes that neither demonstration nor individual laboratory work, during which the pupil follows printed or other directions, does give opportunity for such practice; and that the evidence points to individual self-directed experimentation in problem situations as the method offering the best possibilities of success in obtaining such outcomes.

It is evident that the experimental data we possess point definitely to the superiority of the demonstration method as far as those outcomes that may be measured by the ordinary written tests are concerned. The studies referred to do not furnish us with a satisfactory solution of our problem. A measuring instrument must be devised for determining the educational product unobtainable without the laboratory method. Indeed, we are not certain what procedure should constitute either the laboratory method or the demonstration method. I seriously doubt the wisdom of standardizing to any great extent either method. Teachers vary greatly in their ability to perform experiments or to conduct laboratory periods. Pupil needs also vary. Perhaps laboratory work should not be required of all pupils. The life-motivating influences inherent in these competing methods may ultimately decide the issue for secondary-school work. The question might well be raised, "Which method stimulates maximum pupil interest?"

The reaction of pupils as reported by a study conducted here in New York City in 1927–1928 indicates that the majority of pupils prefer the individual laboratory method. The report of science teaching in New York City emphasized:

1. That the development of the scientific attitude is one of the most important objectives in science teaching in the opinion of New York City teachers.
2. That the majority of science teachers are convinced that the individual laboratory method contributes most toward the development of this attitude.

These statements represent tabulations of opinions. Experimental data available at the present time do not reveal much superiority for the laboratory in this respect. Again no satisfactory method of measuring the scientific attitudes has been developed, although commendable work in this direction is being done by Davis and others in Wisconsin.

Unfortunately, many educational administrators have more faith in so-called scientifically conducted experiments in educational research than the experimenters themselves. The writer does not wish to belittle educational experiments. It is common knowledge, however, that precise instruments for measuring educational products are lacking. On the other hand, many research chemists who require the most careful technics in their own fields abandon their scientific methods when dealing with educational problems.

The educational administrator is confronted with many serious financial problems on every hand. To him the demonstration method represents a possible economy without an apparent decrease in efficiency of instruction. As Dr. Tildsley indicated in the New York City study, the demonstration method falls wonderfully in line with regard to the administration of the science program. Less equipment and larger classes make for economy and ease of administration. The American Chemical Society and similar groups interested in the teaching of secondary-school science should acquaint these administrators with the known facts. Further studies should be encouraged in order to throw light on the problem.

It is interesting to note that the teaching in English, social studies, and other fields during recent years has been developing in the direction of what may be described as a laboratory method. We hear of the library as the English laboratory, the social study laboratory, and the business training laboratory. In science, however, it seems that we have been drifting in the opposite direction. The tendency seems to be toward lightening laboratorial requirements, and toward substituting demonstrations for laboratory experiments, particularly in the case of general science and biological sciences. In New York State general science and elementary biology are taught almost exclusively by the demonstration method. This development has come because of financial difficulties following the World War and because of an unprecedented increase in school enrolments. In the advanced sciences, physics, chemistry, and biology, it has been possible to maintain a relatively high standard of individual laboratory work in spite of some administrative pressure to the contrary. In New York State laboratory work is required in the advanced sciences. In my opinion there is no danger of any modification of these requirements in the near future. I am convinced that the abandonment of the laboratory method at the present time would mean a degeneration of science teaching in the secondary schools.

MEETING OF THE DIVISION OF CHEMICAL EDUCATION

The next meeting of the Division of Chemical Education of the American Chemical Society will take place in Kansas City, April 13th–16th. The main feature of the program will be a symposium on the general subject of Tests and Examinations. Several speakers will discuss the construction and use of standard tests, their advantages and disadvantages. A vigorous discussion is expected. The program will probably cover three and one-half day sessions and the usual Divisional luncheon will be one of the attractive features of the occasion.

N. W. RAKESTRAW, *Secretary*

The LOWEST TEMPERATURES

ENNO WOLTHUIS

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Only a few hundredths of a degree now separate investigators in low-temperature work from the absolute zero. The whole business of attaining extremely low temperatures has today taken on a new color. Whereas formerly the lowest temperatures were reached by boiling liquid helium under reduced pressure, today huge magnets and the rare earths play an important part in arriving at temperatures below one degree absolute.

The method is simply one of sudden demagnetization (adiabatically) of a paramagnetic salt, frequently a rare-earth salt. The substance is its own thermometer since the temperature is a function of the magnetic susceptibility of the salt. Recent reports indicate that a temperature of 0.03 degree absolute has been reached.

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THERE is inherent in man the desire to extend the limits of his knowledge. And when theory dictates a limit, it is quite natural that he strives to reach it. Accordingly, when an absolute zero of temperature was set, it immediately constituted a challenge to the physicist.

The liquefaction of helium was a distinct triumph for those seeking very low temperatures. Then Onnes and Keesom, boiling liquid helium under reduced pressure, succeeded in reaching 0.71 degree absolute. Perhaps the method could have been improved so as to arrive at still lower temperatures in this way. However, within the past few years a new method of attack has been developed. It is our object to select briefly the important contributions to this new phase of low temperature work.

As early as 1895 P. Curie made some valuable observations on the effect of temperature change upon the magnetic susceptibilities of various substances (*1*). It was concluded that, for many substances, the magnetic susceptibility varies inversely with the absolute temperature, particularly at room temperature and above. In 1905, M. Pierre Langevin published an important paper on the theory of magnetism (*2*). This report contains, among other things, a theoretical study of the influence of magnetization upon the temperature of a body. He concluded that, for gases such as oxygen, an appreciable thermal change should accompany the application of a strong magnetic field. In 1921, P. Weiss extended the theory to a study of metals (*3*). He, too, asserted that magnetization produces a rise, and demagnetization a fall, in the temperature of a substance.

The suggestion of using this thermal effect of a magnetic field in obtaining very low temperatures is credited to two independent investigators. W. F. Giauque* first proposed the use of gadolinium sulfate octahydrate in the attainment of temperatures considerably below one degree absolute. In 1927 he published a report of the theory underlying and warranting this proposal (*4*).

* Meeting of the American Chemical Society, California Section, April 9, 1926.

Just prior to the publication of this paper, P. Debye reported independently on his theoretical deductions to the same effect (*5*). One should not fail to mention the important work of Onnes and his associates, whose studies on the magnetic properties of substances at very low temperatures formed a basis for these theoretical developments.

Giauque calls attention to the fact that the effect of a magnetic field upon the ordinary or neutral states of matter cannot compete with the effect of pressure at ordinary temperatures because the former is so minute in comparison with the latter. However, at very low temperatures the magnetic effect becomes significant. In other words, he says, "magnetic effects are large when pressure is no longer practicable as a means of producing a further drop in temperature." Thermodynamics shows that $-T\Delta S$, the heat given out during isothermal magnetization, is appreciable at temperatures of a few degrees absolute. At a temperature of 1.3 degrees absolute a decrease in entropy of 3.3 calories per degree per gram atom of gadolinium is the result of a field of 20,000 gauss.

On the basis of these calculations and others, Giauque proposed a relatively simple procedure for obtaining very low temperatures. First, isothermal magnetization of a substance while it is in contact through gaseous conduction with liquid helium, the latter preferably at reduced pressure. Secondly, adiabatic demagnetization after the space between the substance and the helium has been evacuated. Concerning the working substance to be used, Giauque suggested dysprosium sulfate octahydrate. Dysprosium and holmium salts have also been proposed. These salts, in particular, show large magnetic moments, and are therefore most suitable for use.

These studies were continued with a view to a more precise estimate of the necessary conditions for producing such low temperatures. Giauque and Clark have published some concrete results based upon their study of gadolinium sulfate (*6*). Very briefly, the method is as follows. At zero field strength the total entropy of a substance (excluding nuclear spin effect, and assuming

the ideal case of no interaction between gadolinium atoms) is expressed by:

$$S_T = R \ln 8 + \frac{3.5}{3} \times 10^{-4} T^3$$

If S is the change (reduction) in entropy due to the application of a field, H, at a temperature, T, the total entropy for a given situation is

$$S_{T,H} = R \ln 8 + \Delta S_M + \frac{3.5}{3} \times 10^{-4} T^3$$

(In the case of substances other than the hydrated sulfate, the constant in the T^3 term would be altered.) This total entropy remains constant during an adiabatic demagnetization. Therefore, if the value for ΔS_M is known for a certain temperature and change in field strength, it may be found for another temperature, and the corresponding necessary change in field strength may be computed. In this manner it was found that gadolinium sulfate octahydrate should cool from 10 degrees to 0.5 degree absolute when the magnetic field is reduced from 12,000 to 171 gauss.

The whole process may be given a fairly simple explanation. In the words of de Haas, "A magnetizable body contains a great number of small elementary magnets. When such a body is magnetized these magnets are directed. The part of the entropy belonging to this order is decreased and, the process being supposed isentropic, the part of the entropy connected with the statistical movement must necessarily increase. When, on the contrary, the disorder of the elementary magnets is increased by demagnetization, the part of the entropy connected with the magnetization is increased and the part belonging to the statistical movement is decreased, so that the body is cooled down" (7).

Thus far we have sketched briefly the theory involved. Let us further consider the actual experimental results obtained in the search for absolute zero by this new method. In this country Giauque and his collaborators have done considerable work in obtaining temperatures below one degree absolute. They were actually the pioneers in the experimental verification of the theory. However, we find that the larger part of the work is now being done in the Kamerlingh Onnes Memorial Laboratory at Leiden, The Netherlands. De Haas and others have long been active in the study of magnetic phenomena, and it is quite natural to find them using their powerful magnets in verifying the theory involved in the attainment of very low temperatures.

There are two principal methods for measuring the change in temperature during demagnetization, namely the inductance coil method and the weighing method. The former is the original and more generally used one. However, because the principles underlying the weighing method are more generally understood, we shall discuss it here. The method, as employed by de Haas, is fully described in a recent paper (8). This report contains also a description of the apparatus used. A much simplified sketch is found in Figure 1, to which we shall refer in outlining the experimental method used in the Leiden laboratory.

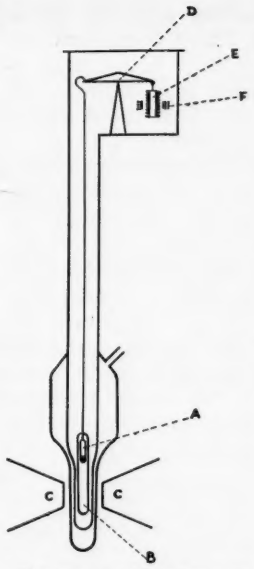

FIGURE 1.—SKETCH OF APPARATUS FOR MEASURING MAGNETIC SUSCEPTIBILITY AT LOW TEMPERATURES

The tube, A, containing the salt, usually a rare earth salt, is placed in another tube, B, surrounded by liquid helium, in such a position that the salt is in the spot of maximum $M(\delta H/\delta X)$ of a large electromagnet, C. A strong magnetic field, often 20,000 gauss, is applied and exerts a force upon the salt. This force is measured by means of a balance, D. One arm of the balance is fastened to the sample by means of a long thin rod; the other arm is attached to a coil, E, itself surrounded by another oppositely wound coil, F, in series with it. The force, then, is measured in terms of amperes of current through the coils, each ampere being equivalent to a certain number of grams, as previously determined.

The substance is thus kept in the strong field until the force upon it is constant, which indicates that the temperature of the salt has finally come down to that of the helium bath. Then suddenly the magnetic field is reduced to a very low value. Immediately force readings are taken, and again at various intervals of time. The force is found to diminish as time goes on, due to a heating up of the substance. This diminution of force with time is shown graphically in Figure 2. Force readings are continued until they no longer show any variation, indicating that the substance has again arrived at the temperature of the surrounding helium.

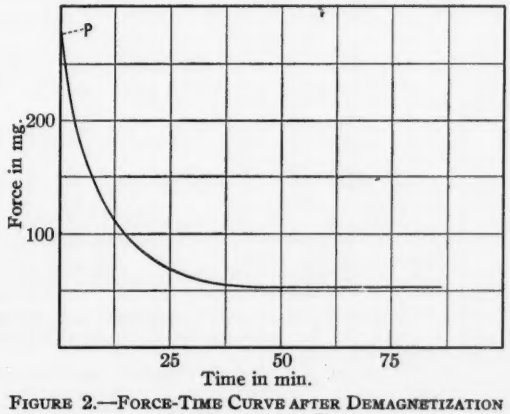

FIGURE 2.—FORCE-TIME CURVE AFTER DEMAGNETIZATION OF A RARE-EARTH SALT

Following the collection of these data, the lowest temperature is computed in the following manner. The lowest temperature corresponds to the point of maximum force, namely the point P in Figure 2. If, then, for a certain substance, the force can be plotted over a measurable range of temperature, a linear extrapolation will indicate the temperature corresponding to the maximum observable force. This is essentially the method used in estimating these lowest of all temperatures. The magnetic susceptibility, therefore, becomes the thermometer when other thermometers fail.

We shall now indicate briefly some of the results obtained. Using gadolinium sulfate octahydrate, Giauque and MacDougall reached a temperature of 0.25 degree absolute as measured by the inductance coil method (*9*). Subsequently de Haas and associates published their results of a study of several different rare-earth salts. Some of their data follow (*10*).

Substance used (mg.)	*Initial field (gauss)*	*Low field (gauss)*	*Maximum force after demagnetization (mg.)*	*Lowest temperature (abs.)*
Cerium fluoride	27,600	4500	295.4	0.27
Dysprosium ethyl sulfate	19,500	350	344.4	0.12
Cerium ethyl sulfate	27,600	850	190.5	0.08

It might be observed that the authors point out that the estimated temperature values obtained by linear extrapolation are the maximum, and that the actual temperatures are very likely lower.

It is generally conceded that the dilution of rare-earth atoms with other atoms is desirable in these experiments, because it prevents the interaction of magnetic atoms. Hence, cerium ethyl sulfate, for example, is preferable to cerium fluoride. Similarly, other rare-earth ethyl salts are now receiving much attention. A recent report from the Leiden laboratory, however, tells of using ordinary potassium chrome alum in the attainment of the lowest temperature to date, namely 0.031 degree absolute (*11*). Likewise Kurti and Simon have reported the use of manganese ammonium sulfate in obtaining a temperature 0.04 degree absolute (*12*).

The question naturally arises whether this method of cooling has any more than a theoretical value. It is true that as a practical cooling device it does not yet seem feasible. However, the magnetic cooling effect is of considerable scientific interest and value. It has been used in studies of electrical and thermal conductivities, heat capacities and quantum states, the interaction of atomic magnets, and the like. Undoubtedly, it will be used to furnish considerable information regarding atomic structures. And, as in all cases of theory, the theoretical lower limit of temperature requires verification.

De Haas and Wiersma, in *Physica*, **2**, 335–40 (1935), have recently reported the use of chrome alum in reaching the temperature of 0.0044 deg. K.

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An OUTLINE *of* ESSENTIALS *for a* YEAR *of* HIGH-SCHOOL CHEMISTRY

REPORT OF THE COMMITTEE ON CORRELATION OF HIGH-SCHOOL WITH COLLEGE CHEMISTRY

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SEVERAL years ago the Division of Chemical Education of the American Chemical Society published a list of Essentials for the help of high-school teachers of chemistry. That list has been useful in the effort to produce a closer correlation between the chemistry taught in preparatory schools and that offered in colleges. It now seems wise to revise and rearrange that list, in order that it may be kept abreast of changing thought and methods in chemical education.

The present committee representing the viewpoints of both the high school and the college believes that objectives in the teaching of high-school chemistry should differ fundamentally from those which characterize an elementary college course. In the high school the viewpoint should be informational, broadening, and cultural as contrasted with the technical, professional, and specialization attitude which is unavoidable in the college. As a consequence we urge teachers in preparatory classes to present courses which are planned primarily to meet the needs and interests of their pupils.

It must of course be recognized that many high-school pupils are planning to enter college and accordingly they must be prepared to pass the entrance examinations and to show a reasonable understanding of the fundamentals of chemistry. We do not believe that a separate college entrance course is necessary or advisable, since there are certain foundational topics which must be taught in any type of course in chemistry.

The committee has undertaken to prepare an outline which will meet the needs of the pupil who enters college and of the one who goes directly into the active affairs of life. We have attempted to include in our basic list (large type) only those vitally essential topics which should be presented in all elementary courses. In order to give flexibility and adaptability, additional topics are appended in smaller type. These latter topics are only suggestions. Some of them have already been taught in some previous science course, and others will be taught in college. It is expected that teachers will select only those which circumstances warrant in order to adapt the training to the particular needs and interests of the particular locality. It is expected that other supplementary topics will be added to the list by the teacher.

The committee makes the following suggestions to aid the high-school teacher in developing the topics listed below:

1. To show the service of chemistry to the home, to health, to medicine, to agriculture, to industry; in a word, to show the service of chemistry to the country.
2. To develop this service in chemistry around certain minimum fundamental topics, and, in doing so, to see that these minimum requirements are so well taught that they may be built upon, if required, as a foundation in college.
3. To train the student in keen observation and exact reasoning, and in the scientific attitude of mind.
4. To develop a careful correlation between recitation and experiment.
5. To encourage students to keep notebooks which shall be an accurate record of laboratory experience expressed in concise, clear English.
6. To build upon the earlier science courses and knit them together wherever possible.
7. To encourage students to use reference books and scientific periodicals, in addition to their textbooks.
8. To help pupils to find themselves—*i. e.*, to discover whether or not they have an aptitude for further study in chemistry or applied science, and, if so, to encourage such students to continue their study of science in university or technical school.
9. To stress the general principles involved in the specific cases studied, and to assure the pupils' mastery of each principle.
10. To use well-established principles of psychology as far as they can be applied to students of high-school chemistry.

TOPICS FOR A STANDARD HIGH-SCHOOL COURSE IN CHEMISTRY†††

UNIT I—INTRODUCTION

1. Brief history of the development of chemistry.
2. The meaning of present-day chemistry.
3. How to study chemistry.
4. A simple consideration of matter including the solid, liquid, and gaseous states.

Experiment 1: To learn to handle apparatus properly; using the Bunsen burner; cutting, bending, and annealing glass; weighing; decanting; filtering, etc.

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††† The teachers are advised to use their own order in developing these topics, realizing that the material may be grouped around other central ideas than those shown in the units.

UNIT II—DISPERSIONS

SECTION 1: DISTRIBUTION OF WATER

(*a*). General distribution.
(*b*). Physical properties of water: color, odor, taste, density, boiling point, freezing point.
(*c*). Distribution of water in foods.
(*d*). Distribution of water in crystals: hydrates, water vapor, deliquescence and efflorescence.

Experiment 2: To determine the percentage of water of hydration in a hydrated salt; *e. g.*, copper sulfate, barium chloride, selenite.

SECTION 2: DISPERSIONS IN WATER

(*a*). Definition of molecule.
(*b*). Different types of dispersions in water; molecular, colloidal, suspensoid.
(*c*). Molecular dispersion or solution: solvent, solute, saturated solution, process of solution, degrees of solubility, factors affecting the solubility of a substance.
(*d*). Suspension.

Experiment 3: To study solutions, solvent power of water, saturation.

(*e*). Removal of dispersed material in water, or purification: by boiling, distillation, filtration, chemical treatment (chlorine).

Experiment 4: Distillation.

SECTION 3: COLLOIDAL DISPERSIONS

(*a*). Terms used in colloidal field: dispersed phase, dispersion medium, sol, gel, emulsoid, suspensoid, Brownian movement.
(*b*). Preparation of colloidal dispersions.
(*c*). Possible colloidal dispersions in the three states of matter.
(*d*). The use and importance of dispersions.

UNIT III—CHEMICAL CHANGE, ELEMENTS, COMPOUNDS AND MIXTURES

SECTION 1: EXAMPLES OF CHEMICAL CHANGE

(*a*). Composition of water, quantitatively by electrolysis, and qualitatively by synthesis from copper oxide or by burning hydrogen.

Experiment 5: To study the electrolysis of water. (Lecture experiment.)

Experiment 6: To reduce copper oxide by hydrogen (or illuminating gas).

(*b*). Preparation of oxygen from potassium chlorate (use of a catalytic agent).

Experiment 7: To prepare oxygen from potassium chlorate, to study its properties, and to recover the potassium chloride and manganese dioxide.

(*c*). Preparation of hydrogen.

Experiment 8: To study the action of metals (iron and zinc) on dilute hydrochloric and sulfuric acids: properties of hydrogen.

Experiment 9: To prepare hydrogen from water by means of active metals.

(*d*). Preparation of nitrogen from ammonium nitrite.
(*e*). Contrast of physical and chemical change.

(*f*). Contrast of elements and compounds.
(*g*). Contrast of elements, compounds, and mixtures.

Experiment 10: To distinguish between a mixture and a compound.

(*h*). Kinds of chemical change: synthesis (composition); decomposition; simple replacement (substitution); double replacement (metathesis).
(*i*). Conditions under which chemical reactions take place—gas evolved, precipitate, un-ionized product (water).

SECTION 2: AIR AS A MIXTURE

(*a*). Percentage of oxygen and nitrogen by volume.

Experiment 11: To determine the respective percentages of oxygen and of nitrogen in air. (Lecture experiment.)

(*b*). Tests for water vapor and for carbon dioxide in air.
(*c*). Liquid air: principle of preparation and source of oxygen and nitrogen.
(*d*). Four proofs that air is a mixture and not a compound.

SECTION 3: USE OF CHEMICAL CHANGE IN FIXING ELEMENTS

(*a*). Fixation of oxygen (formation of oxides in air and in oxygen); oxidation; oxygen + carbon; oxygen + sulfur; oxygen + phosphorus; oxygen + copper.

Experiment 12: To fix oxygen to carbon, sulfur, phosphorus, and copper.

Experiment 13: To determine the change in weight on heating a metal in air.

(*b*). Fixation of hydrogen: hydrogen + oxygen; hydrogen + chlorine; hydrogen + nitrogen.

Experiment 14: To fix hydrogen to oxygen, to chlorine, and to nitrogen.

(*c*). Fixation of nitrogen: nitrogen + oxygen; nitrogen + hydrogen.
(*d*). Combustion as a chemical change and as illustrated by (*a*), (*b*), (*c*); kindling temperature; spontaneous combustion.
(*e*). Energy change treated qualitatively; heat, light, electrical energy.

Experiment 15: To study the relation of energy to chemical changes as illustrated by the evolution or absorption of heat, light, and electricity in chemical reactions.

(*f*). Cycles in nature brought about through chemical changes: carbon dioxide cycle; nitrogen cycle.

UNIT IV—THE STRUCTURE OF MATTER

SECTION 1: THE ELECTRICAL THEORY OF MATTER

(*a*). Definition of electron, proton, and neutron.
(*b*). Location in atom.
(*c*). Relative mass and charge of each.
(*d*). The electronic structures of some elements such as hydrogen, helium, nitrogen, and oxygen.
(*e*). Chemical changes involve a transfer or sharing of electron, illustrated by formation of such compounds as sodium chloride and methane.
(*f*). Significance of number of electrons in outer orbit.
(*g*). Relation between valence and the number of electrons lost, gained, or shared by elements.

Experiment 16: To determine the weight of magnesium (or aluminum) that displaces one gram of hydrogen.

(*h*). Contrast of the electronic theory of matter and Dalton's atomic theory.

SECTION 2: LAWS, HYPOTHESES, THEORIES

(*a*). Law of conservation of mass.
(*b*). Law of definite composition (proportion).

Experiment 17: To determine the weight of copper (or nickel) that combines with one gram atomic weight of sulfur.

(*c*). Law of Boyle and Law of Charles, treated briefly with special reference to gases, not experimentally, but rather their application to the interpretation of change of volume.

(*d*). Temperature and pressure corrections for volumes of gases.
(*e*). Law of Gay-Lussac and Avogadro's hypothesis.

UNIT V—SYMBOLS, EQUATIONS, WEIGHT RELATION, AND VOLUME RELATION

SECTION 1: ATOMIC AND MOLECULAR WEIGHTS

(*a*). Atomic weights (not their derivation), use in performing chemical calculations.

(*b*). Molecular weights as explained by Law of Gay-Lussac and Avogadro's hypothesis.

(*c*). Molecular weights calculated from atomic weights of constituents.

SECTION 2: SYMBOLS, FORMULAS, AND VALENCES

(*a*). Symbols and formulas, their meaning and use in writing equations.
(*b*). Rules for the naming of chemical substances.
(*c*). Valence, including electronic interpretation.

SECTION 3: EQUATIONS AND PROBLEMS

(*a*). Equations, and their use in expressing chemical changes, including gravimetric and volumetric equations.
(*b*). Problems involving: (1) percentage composition, (2) weights of substances and volumes of gases concerned in chemical reactions, and (3) the laws of gases.
(*c*). Kinds of chemical changes: (1) oxidation and reduction as illustrated by combination, decomposition, simple replacement (substitution), including electronic interpretation of each: (*a*) double replacement (metathesis).
(*d*). Formulas and writing of equations for reactions already studied.

UNIT VI—THE PERIODIC CLASSIFICATION

SECTION 1: THE ELECTRONIC STRUCTURE OF THE ATOM

(*a*). The proton and neutron as units of mass in building atoms.
1. Atomic weights and isotopes.
2. Atomic numbers and their importance.

SECTION 2: THE PERIODIC CLASSIFICATION ACCORDING TO ATOMIC NUMBERS

(*a*). The atomic number of an element determines its properties.
(*b*). The arrangement in periods of eight and eighteen.
(*c*). The relation between valence and the group in which an element falls.
(*d*). The positions of the metallic and non-metallic elements in the table.
(*e*). The gradual change in acid and basic properties as we pass from an element with one atomic number to the next in order.
(*f*). Location of amphoteric elements.
(*g*). Significant values of the periodic classification.

SECTION 3: A STUDY OF THE HALOGEN GROUP TO SHOW THE MEANING OF GROUP RELATIONS

This is to be done as a demonstration by the teacher and to be carried as far as the teacher thinks advisable or as far as time permits.

SECTION 4: THE HISTORY OF THE PERIODIC CLASSIFICATION

(*a*). Döbereiner's triads.
(*b*). Newland's octaves.
(*c*). Mendeléef and Meyer classification.

UNIT VII—ACIDS, BASES, SALTS, AND IONIZATION

SECTION 1: ACIDS

(*a*). Preparation of acids from non-metallic oxides (acid anhydrides): sulfur dioxide, phosphorus pentoxide, carbon dioxide, and nitrogen dioxide.

Experiment 18: To prepare sulfur dioxide: (1) by burning sulfur; (2) from a sulfite and an acid; and to study the properties of a gas evolved.

(*b*). General rules for preparation of acids.
(*c*). Preparation of sulfuric acid, nitric acid, hydrochloric acid, and hydrogen sulfide.

Experiment 19: To prepare nitric acid. (Lecture experiment.)

Experiment 20: To study the properties of nitric acid, including its action with copper.

Experiment 21: To prepare sulfuric acid from sulfur dioxide by the use of an oxidizing agent and to study its properties.

Experiment 22: To prepare hydrogen sulfide and to study its properties.

Experiment 23: To prepare hydrogen chloride (hydrochloric acid) and to study its properties.

(*d*). General properties: of acids: tests, action on litmus, etc.
(*e*). Principal use of each acid given above.

SECTION 2: BASES

(*a*). Preparation of bases from such metallic oxides (basic anhydrides) as sodium oxide and calcium oxide; ammonia.

Experiment 24: To study the preparation of typical basic and acidic oxides, their action on water, and their interaction.

(*b*). General rules for preparation of (1) soluble bases, (2) insoluble bases.

Experiment 25: To prepare sodium hydroxide, calcium hydroxide, ammonium hydroxide, aluminum hydroxide, ferric hydroxide, zinc hydroxide.

(*c*). General properties of bases: taste, action on litmus, etc.

(*d*). Principal use of each base prepared.

SECTION 3: SALTS

(*a*). General methods for preparation of salts: neutralization, acid plus metal, acid plus salt of a more volatile acid, acid plus oxide of metal or acid plus carbonate, direct combination.

Experiment 26: To study quantitatively by titration the neutralization of tenth normal solutions of sodium hydroxide and hydrochloric acid. (Lecture experiment.)

Experiment 27: To study the preparation of soluble salts and the isolation of the product.

Experiment 28: To study the preparation of insoluble salts by precipitation.

(*b*). General properties of salts: taste, action on litmus, etc.

(*c*). Uses of salts prepared.

Experiment 29: To test for nitrate, sulfide, sulfate, chloride, and carbonate ions.

Experiment 30: To study the colors of ions. (Lecture experiment.)

SECTION 4: IONIZATION THEORY

(*a*). The effect of acids, bases, and salts on the freezing and boiling points and conductivity of their solutions.

Experiment 31: To study solutions of electrolytes and non-electrolytes.

(*b*). The theory of ionization and how it helps in the explanation of the phenomenon noted in (*a*).

(*c*). Contrast Arrhenius' theory with other theories on ionization.

(*d*). How the ionic theory explains electrolysis, and its electronic interpretation.
(*e*). Activity of acids and bases and neutralization explained by the ionization theory.
(*f*). Acid and base defined in terms of ions: test for hydrogen ions and hydroxyl ions. (Arrhenius theory.)

(*g*). Acid and base defined in terms of loss or gain of protons (Brönsted theory.)

(*h*). Atom and ion distinguished and the electronic interpretation.

SECTION 5: ELECTROMOTIVE SERIES

(*a*). What is meant by the electromotive or displacement series.
(*b*). The electronic factors which determine the place of a metal in the displacement series, electronegativity.

(*c*). The arrangement of the elements in the series.

Experiment 32: To study the displacement (electrochemical series) of certain common metals.

(*d*). The hydrogen electrode and its use.
(*e*). Measuring the hydrogen-ion concentration and its practical applications.

UNIT VIII—THE NATURE OF NON-METALLIC ELEMENTS

SECTION 1: GENERAL OCCURRENCE AND PREPARATION OF SOME TYPICAL NON-METALLIC ELEMENTS

(*a*). Oxygen—Occurrence; preparation: electrolysis of water; potassium chlorate (use of catalytic agent); industrial. Review Unit III, Section 1, (*a*) and (*b*).
(*b*). Hydrogen—Occurrence; preparation: electrolysis of water; action of certain metals (*e. g.*, sodium) on water; replacement in acids by metals; industrial. Review Unit III, Section 1, (*a*) and (*c*).

(*c*). Nitrogen—Occurrence; preparation. Review Unit III, Section 1, (*d*).

(*d*). Sulfur—Occurrence; extraction: American method (Frasch method). Allotropic forms: crystalline and amorphous.

Experiment 33: Allotropic forms of sulfur.

(*e*). Phosphorus—Occurrence; preparation; properties and uses.

(*f*). Chlorine—Occurrence; preparation (electrolysis of water solution of sodium chloride); one laboratory method (hydrochloric acid with manganese dioxide); an industrial method; bleaching powder plus an acid.

Experiment 34: To prepare chlorine and to study its properties.

SECTION 2: THE GENERAL PROPERTIES OF THE NON-METALLIC ELEMENTS (INTERPRETED ON THE BASIS OF ELECTRONIC STRUCTURE) AND THEIR USES (ON THE BASIS OF PROPERTIES)

(*a*). Oxygen—Physical properties: color, odor, solubility in water, weight relative to air.
Chemical properties: formation of oxides in air, and oxidation and combustion, including gravimetric interpretation. Review Unit III, Section 1, (*a*) and (*b*).
Uses: necessary to life.

(*b*). Hydrogen—Physical properties: as with oxygen.
Chemical properties: burns in air, explosive mixtures, reduction by hydrogen including electronic interpretation. Review Unit III, Section 1, (*a*) and (*c*).
Uses: oxyhydrogen flame; balloons; hydrogenation of oils.

Hydrogen peroxide: properties and uses.

(*c*). Nitrogen—Physical properties: as with oxygen.
Chemical properties: non-supporter of combustion; general inactivity, negative test. Review Unit III, Section 1, (*d*).
Uses: nitrogen fixation, as illustrated by plants. Synthesis of ammonia and oxides of nitrogen.

(*d*). Sulfur—Properties electronically interpreted and compared with those of oxygen, as in direct combination with hydrogen, metals, etc.
Uses: vulcanizing rubber, making matches, making sulfur dioxide and sulfuric acid.

(*e*). Chlorine—Physical properties: as with oxygen.
Chemical properties: direct combination with other elements to form chlorides, and its electronic interpretation; tests for chloride ion; comparison with oxygen. Review Unit VIII, Section 1, (*f*).
Uses: bleaching and disinfecting.

UNIT IX—CARBON, CARBON DIOXIDE, AND CARBON MONOXIDE

SECTION 1: CARBON

(*a*). The electronic structure of carbon and the boundary line between metals and non-metals.

(*b*). Occurrence.
General distribution.
Allotropic forms: diamond and graphite (crystalline), amorphous forms.

(*c*). Commercial preparation of useful forms: graphite, charcoal, lampblack, coke, boneblack.

(*d*). Uses: common fuels containing carbon or carbon compounds, operation of household stoves and furnaces, reduction by carbon, decolorizer, adsorbent.

Experiment 35: To study the adsorptive and reducing powers of carbon.

SECTION 2: CARBON DIOXIDE

(*a*). Occurrence: relation to plant and animal life.

(*b*). Preparation: burning carbon or a carbon compound, action of acid on a carbonate, heating a carbonate.

Experiment 36: To prepare carbon dioxide and to study its properties.

(*c*). Properties:
Physical: as with oxygen.
Chemical: non-supporter of combustion, rôle of carbon dioxide in nature, plant growth, test for carbonate ion.

(*d*). Uses: refrigerant, beverages, fire extinguisher, leavening agent in bread making.

Experiment 37: To study the action of baking powders and to determine their ingredients.

SECTION 3: CARBON MONOXIDE

(*a*). Preparation (teachers' demonstration) from formic or oxalic acid, reduction of carbon dioxide by carbon.

Experiment 38: To prepare carbon monoxide and to study its properties. (Lecture experiment.)

(*b*). Properties:
Physical: as with oxygen.
Chemical: combustibility, reducing power.

(*c*). Poisoning by carbon monoxide.

Experiment 39: To study the structure of flame; the oxidizing and reducing flame.

(*d*). Use: reducing agent, industrially; constituent of water gas, coal gas, and producer gas.

(*e*). Manufacture and uses of illuminating and fuel gases.

UNIT X—THE NATURE OF METALLIC ELEMENTS

SECTION 1: GENERAL FACTS ABOUT METALLIC ELEMENTS

(*a*). Occurrence: free, combined.

(*b*). General methods of extraction; roasting of non-oxide ore, reduction of oxide by carbon or hydrogen or an easily oxidized metal like aluminum; electrolysis of an hydroxide or a chloride; electronic interpretations of these methods.

(*c*). Action of air, water (including steam), and dilute acids on the common metals.

(*d*). General properties, including the power to conduct heat and electricity.

SECTION 2: A STUDY OF TYPICAL METALLIC ELEMENTS: SODIUM, CALCIUM, IRON, AND ALUMINUM

(*a*). Sodium—Occurrence—NaCl.
Preparation—electrolysis.
Physical properties: metallic luster, hardness, color.
Chemical properties: flame test, action with water, with chlorine.

Experiment 40: To study the action of sodium on water, with recognition of the product formed.

Experiment 41: To test for potassium, sodium, barium, strontium, and copper by flame coloration.
Uses: in sodium compounds.

(*b*). Calcium.

1. Occurrence only.
2. Industrial. Uses of its compounds (carbonate, hydroxide, oxide, sulfate, and phosphate).

Experiment 42: To study the preparation and properties of calcium oxide, hydroxide, and carbonate.

3. Contrast permanently hard water with temporarily hard water.

Experiment 43: To study hard water and one method of softening each type.

(*c*). Iron.

1. Metallurgy (extraction from oxide ores; blast furnace; pig iron).
2. Use of cast iron: castings.
3. Steel: manufacture.
4. Protective coatings to prevent corrosion of iron and steel: tin (tinware), zinc (galvanized iron), enameled ware, paint.

5. Compounds of iron: ferrous and ferric compounds; oxidation and reduction of iron compounds, including change of valence and electronic interpretation.

Experiment 44: To study the change from ferrous chloride to ferric chloride, and vice versa; oxidation, reduction; to test for the ferrous and for the ferric ion.

(*d*). Aluminum.

1. Preparation as compared with sodium and calcium.
2. Properties and uses (oxidation, action with acids and bases, density, strength).

Experiment 45: To study the action of acids and alkalies on aluminum.

Experiment 46: To study the use of aluminum hydroxides in purifying water.

SECTION 3: ALLOYS

(*a*). The nature of alloys.
(*b*). How desirable properties are obtained.
(*c*). Theory of alloys.

UNIT XI—ORGANIC CHEMISTRY

SECTION 1: CHARACTERISTIC ORGANIZATION OF CARBON COMPOUNDS

(*a*). Old and new definitions of organic chemistry.
(*b*). Composition: elements present in most organic compounds.
(*c*). Formula correspondence between inorganic and organic substances: organic radical to metal; ether to oxide; alcohol to hydroxide; hydrocarbon to hydride; organic acid to mineral acid; and ester to salt.
(*d*). Structural (graphic) formulas.

SECTION 2: HYDROCARBONS

(*a*). Classes of hydrocarbons: methane, ethylene, acetylene, and benzene series.
(*b*). Brief treatment of the occurrence, preparation, properties, and uses of methane, ethane, ethylene, acetylene, and benzene.
(*c*). Industrial sources of certain hydrocarbons and accompanying side products.

1. Destructive distillation of wood: methanol, acetic acid, charcoal.
2. Destructive distillation of coal: gas, ammonia, benzene, tar, and coke.

Experiment 47: To study the destructive distillation of wood and soft coal.

3. Distillation of petroleum: benzine, gasoline, kerosene, lubricating oil, fuel oil, vaseline, paraffin.

SECTION 3: ALCOHOLS

(*a*). Relation of alcohols to the corresponding hydrocarbons.
(*b*). Preparation, properties, and uses of methanol and ethanol.

SECTION 4: ORGANIC ACIDS

(*a*). Brief treatment of the sources, industrial preparation, properties, and uses of acetic acid.
(*b*). Brief mention of formic, oxalic, lactic, tartaric, citric, and stearic acids.
(*c*). A few metallic salts of organic acids.

SECTION 5: ESTERS

(*a*). Composition.
(*b*). Brief treatment of the preparation, properties, and uses of ethyl acetate, fats, and oils.
(*c*). Esters as ingredients of animal fats and of many artificial flavors.

SECTION 6: CARBOHYDRATES

(*a*). Composition.
(*b*). Brief treatment of the sources, industrial preparation, properties, and uses of cane sugar, glucose, starch, and cellulose.

SECTION 7: FOODS

(*a*). Chemical elements in foods.
(*b*). Ingredients of foods: fats, oils, carbohydrates, proteins, mineral salts, water, and vitamins.
(*c*). Foods that contain high percentages of each ingredient.

SECTION 8: MISCELLANEOUS ORGANIC COMPOUNDS

(*a*). Composition, preparation, properties, and cleansing action of soap.
(*b*). Preparation (briefly), properties, and uses of aniline, nitrobenzene, and nitroglycerin.
(*c*). Composition, properties, and uses of formaldehyde.
(*d*). Preparation, properties, and uses of ethyl ether.
(*e*). Relation of halogen derivatives to the corresponding hydrocarbons.
(*f*). Properties and uses of chloroform and iodoform.

ELEMENTS *of the* QUANTUM THEORY*

IX. THE HELIUM ATOM. PART II. THE VARIATIONAL METHOD

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MATHEMATICAL FORMULATION

THE variational (or Ritz) method has been used extensively in classical physics, especially in the field of dynamics, where its application is at least as old as d'Alembert's principle of virtual displacements.† However, the most important applications of the method were made by Lagrange and Hamilton. The principle formulated by the latter is regarded as one of the most fundamental generalizations in physics, and may be stated in the following form.

If we compare any dynamical path (that is, one which proceeds in accordance with the laws of dynamics) with *varied paths*, which have the same termini (in the configuration space) and which are described in the *same time*, then the time integral of the function $L = L(q_i, \dot{q}_i, t)$, known as the Lagrangian or kinetic potential function, is an *extremum* (that is, *either a maximum or minimum*) for the dynamical path.

The function L is defined by the relation,

$$L = T - V \tag{357}$$

where T denotes the kinetic, and V the potential energy. If $q_1, q_2, \ldots, q_f$ denote the f generalized coördinates of the system, then $T = T(q_i, \dot{q}_i)$, and $V = V(q_i)$, that is, the potential energy is a function of the f coördinates only. In the case of a *conservative system*,

$$E = T + V = \text{a constant}$$

* This is the twelfth of a series of articles presenting a more detailed and extended treatment of the subject matter covered in Dr. Dushman's contribution to the symposium on Modernizing the Course in General Chemistry conducted by the Division of Chemical Education at the eighty-eighth meeting of the American Chemical Society, Cleveland, Ohio, September 12, 1934. The author reserves the right to publication in book form.

† This principle is discussed in A. G. WEBSTER's "The dynamics of particles and of rigid, elastic and fluid bodies," B. G. Teubner, Leipzig, 1912, p. 63. This is an invaluable reference on classical mechanics.

The following references also contain a discussion of classical mechanics:

L. PAULING AND E. B. WILSON, "Introduction to quantum mechanics," McGraw-Hill Book Company, Inc., New York, 1935.

J. H. JEANS, "Theoretical mechanics," Ginn and Company, Boston, 1907.

W. V. HOUSTON, "Principles of mathematical physics," McGraw-Hill Book Company, Inc., New York, 1934.

S. DUSHMAN, Taylor's "Treatise on physical chemistry," Vol. 2, p. 1264, D. Van Nostrand Co., New York, 1930.

We can express Hamilton's principle in the variational form

$$\delta\int_{t_0}^{t_1} L dt = \delta\int_{t_0}^{t_1}(T - V)dt = 0 \qquad (358)$$

where the symbol δ is used to indicate any arbitrary (small) variation, and in any treatise on the calculus of variation* it is shown that the conditions which must be satisfied in order that the integral in (358) shall be an extremum are given by the f equations, *one for each generalized coördinate*, of the form

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0 \qquad (359)\dagger$$

where $\dot{q}_i = dq_i/dt$, and it will be observed that $\partial L/\partial q_i$ is the *partial* differential coefficient of L with respect to the particular variable q_i.

The last equation is known as *Euler's equation* in the calculus of variation, and also as *Lagrange's equation* in dynamics. It will be observed that in equation (358) the *variation applies to a function, L,* and *not to a coördinate* (as in ordinary calculus), and it is because of this generality of the criterion (359) that the latter has proved so extremely useful in solving many problems in classical dynamics.

It was therefore not unreasonable to expect that the method of variations would find equally important application in connection with the problems of quantum mechanics. In fact, the most striking feature about the whole history of the development of theoretical physics during the past two hundred years has been the continuous extension of concepts. The experimental discoveries always seem to demand revolutionary changes in ideas and yet, when in the course of time these observations are arranged in a logical frame, it is found that many of the concepts held previously require only a slight modification, or extension, in order to be able to reconcile them with the new facts.

In the case of quantum mechanics it is readily shown that the *S. equation is essentially the Euler differential equation* which must be satisfied in order that a certain definite integral (which corresponds to the total energy) shall be a minimum.‡ Hence, instead of attempting to solve the S. equation in a particularly difficult case, it may be much more feasible to introduce one or more arbitrary parameters into the expression for the corresponding variational integral. By investigating the effect of variations in the values of these parameters, on the value of the integral, it is then possible to determine a minimum value for the latter, that is, a minimum value for the eigenvalue which corresponds to the given S. equation for a particular energy state.

Let us consider first the S. equation in the *operator* form,

$$H\phi = \left(-\frac{1}{\alpha^2}\nabla^2 + V\right)\phi = E\phi \qquad (360)$$

where $\alpha^2 = 8\pi^2\mu/h^2$, and H, known as the *Hamiltonian*, designates the operator in the brackets. Multiplying both sides by $\bar{\phi}$ and integrating over the configuration space, the result is

$$\int\bar{\phi}H\phi d\tau = \int\bar{\phi}E\phi d\tau = E\int\bar{\phi}\phi d\tau$$

where $d\tau$ is the element of volume in this space. Hence,

$$E = \frac{\int\bar{\phi}H\phi d\tau}{\int\bar{\phi}\phi d\tau} \qquad (361)$$

For normalized functions, the denominator in (361) is equal to unity, and $E = \int\bar{\phi}H\phi d\tau$, where ϕ is an eigenfunction for the given S. equation. Suppose, however, that we do not know the exact form of ϕ which should be used to solve equation (360). We may then make a more or less shrewd guess as to the form of the function. Let ψ designate this new function, and let

$$\left.\begin{aligned} I &= \int\bar{\psi}H\psi d\tau \\ \text{and} \quad N &= \int\bar{\psi}\psi d\tau \end{aligned}\right\} \qquad (362)$$

Then, as shown in the following section, the minimum value of I, which we shall denote by M, is always *greater* (more positive) than the true eigenvalue for the corresponding S. equation. That is,

$$\frac{\int\bar{\psi}H\psi d\tau}{\int\bar{\psi}\psi d\tau} = \frac{M}{N} \geqq E \qquad (363)$$

or

$$\int\bar{\psi}H\psi d\tau - E\int\bar{\psi}\psi d\tau \geqq 0$$

For $\psi = \phi$, the correct eigenfunction, the expression on the left-hand side of the last equation is equal to zero.

To demonstrate the validity of (363) we proceed as follows:**

If $E^0 = M/N$ = minimum, then

$$0 = \delta E^0 = \delta\left(\frac{M}{N}\right) = \frac{\delta M}{N} - \frac{M\delta N}{N^2} = \frac{1}{N}(\delta M - E^0\delta N)$$

Hence

$$\delta M - E^0\delta N = 0$$

* The simplest treatment with which the writer is familiar is in the small volume by W. E. BYERLY, "Introduction to the calculus of variations," Harvard Univ. Press, Cambridge, 1920.

† In most cases it will be found that the integral which satisfies the differential equation (359) is a minimum. However, the proof of this conclusion would involve much more tedious mathematics.

‡ This was pointed out by E. SCHROEDINGER in his first paper on "Quantization as an eigenvalue problem," *Ann. Physik*, [4], 79, 361 (1926).

** A proof of this theorem was first given by C. ECKART, *Phys. Rev.*, 36, 878 (1930). For the proof given in the text the writer is indebted to Dr. F. Seitz.

That is,

$$\int(\delta\bar{\psi})H\psi d\tau + \int\bar{\psi}H(\delta\psi)d\tau - E^0\int(\delta\bar{\psi})\,\psi d\tau - E^0\int\bar{\psi}\delta\psi d\tau = 0$$

or

$$\int(\delta\bar{\psi})(H - E^0)\psi d\tau + \int\bar{\psi}(H - E^0)\delta\psi d\tau = 0 \qquad (364)$$

Since $\delta\psi$ is arbitrary, let us replace it by $i\delta\psi$.* Hence, since $\bar{\psi}\psi = |\psi|^2$, a real function, we must replace $\delta\bar{\psi}$ by $-i\delta\psi$, in order that the product $(-i\delta\bar{\psi})(i\delta\psi)$ shall be real. Consequently, (364) becomes,

$$-i\int(\delta\bar{\psi})(H - E^0)\psi d\tau + i\int\bar{\psi}(H - E^0)\delta\psi d\tau = 0$$

Dividing both terms by i, and comparing the resulting equation with (364), it follows that the latter can be valid only if *each integral vanishes identically.*† Hence,

$$(H - E^0)\psi = 0 \qquad (365)$$

which shows that E^0 is an eigenvalue corresponding to the function ψ.

These considerations show that the S. equation is the Euler condition which must be satisfied in order that the integral I in (362) shall be a minimum. The latter may also be expressed in another form, in which it has been used quite frequently by writers on quantum mechanics.

Referring to equation (360), which is merely the S. equation, let us consider the case in which ϕ as well as V are functions of the Cartesian coördinates, x, y, z, and ϕ is a real function. (This limitation to real functions and rectangular coördinates simplifies the mathematics but does not detract from the general validity of the conclusions.) Then,

$$\phi H\phi = \phi\left(-\frac{1}{\alpha^2}\nabla^2\phi + V\phi\right) = -\frac{\phi}{\alpha^2}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}\right) + V\phi^2$$

But

$$\frac{\phi\partial^2\phi}{\partial x^2} = \frac{d}{dx}\left(\frac{\phi\partial\phi}{\partial x}\right) - \left(\frac{\partial\phi}{\partial x}\right)^2$$

Hence, designating $dxdydz$ by dv,

$$\int\phi H\phi dv = \frac{1}{\alpha^2}\int\left\{\left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial y}\right)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2\right\}dv - \frac{1}{\alpha^2}\left[\frac{\phi\partial\phi}{\partial x} + \frac{\phi\partial\phi}{\partial y} + \frac{\phi\partial\phi}{\partial z}\right] + \int V\phi^2 dv$$

where the limits of integration are $x = y = z = \pm\infty$. Evidently, the expression in the brackets must vanish since $\phi = 0$ at the limits of integration. Hence, the integral to be minimized is

$$I = \frac{1}{\alpha^2}\int\left[\left\{\left(\frac{\partial\phi}{\partial x}\right)^2 + \left(\frac{\partial\phi}{\partial y}\right)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2\right\} + V\phi^2\right]dxdydz$$

subject to the condition, $\int\phi^2 dxdydz = 1$.

This may also be written in the form

$$I - E^0 = \frac{1}{\alpha^2}\int\left[\sum\left(\frac{\partial\phi}{\partial q}\right)^2 - (E^0 - V)\phi^2\right]dxdydz \qquad (366)$$

= minimum, where q denotes x, y, or z.

Thus the S. equation is the differential equation which must be satisfied in order that the integral in equation (366) shall be a minimum.

The form of this integral indicates a method by which it may be derived formally from the Hamiltonian expression for E in classical dynamics.

If we write the expression for E in the form

$$E = T + V$$

where T = kinetic energy, and V = potential energy, then in terms of rectangular coördinates,

$$V = V(x, y, z)$$

and

$$T = \frac{\mu}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$= \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2)$$

where p_x = momentum along x-axis, $= \mu\dot{x}$, and similarly for p_y and p_z.

Hence we can write the expression for the total energy in the Hamiltonian form,

$$E = H(p_i, q_i)$$

where q_i designates x, y, z, and p_i, the corresponding component of momentum.

Now let us replace p_x by $\frac{h}{2\pi}\frac{\partial\phi}{\partial x}$, and similarly for p_y and p_z. Then we obtain the expression

$$\frac{h^2}{4\pi^2}\cdot T\left\{\frac{1}{2\mu}\sum\left(\frac{\partial\phi}{\partial x}\right)^2\right\}$$

which is identical with the first term in the integrand of equation (366).

This may be extended to any system for which the total energy is expressed in the Hamiltonian form, that is, as a function of the f generalized coördinates, $q_1 \ldots q_f$, and canonically conjugated momenta, $p_1 \ldots p_f$.

Let

$$E = H(p_i, q_i) = T(q_i, p_i) + V(q_i) \qquad (367)$$

Under these conditions the element of volume is given by

$$d\tau = \sqrt{A}\cdot dq_1 \ldots dq_f$$

where $\sqrt{A}$ is known as the "discriminant,"‡ and therefore the integral to be minimized is

$$I = \int\left\{\frac{h^2}{4\pi^2}\cdot T\left(q_i, \frac{\partial\phi}{\partial q_i}\right) + V\phi^2\right\}d\tau \qquad (368)$$

* This part of the proof is taken from notes on lectures delivered by P. A. M. Dirac at Princeton University in 1931.

† An operator β, such that $\bar{\psi}\beta\psi = \psi\beta\bar{\psi}$ is known as *Hermitian* or self-adjoint. Evidently H or $(H - E)$ is an operator of this type.

‡ This was discussed in Chapter V-A in connection with the form of the Laplacian operator. The discriminant is thus identical in the case of three coördinates, with the magnitude $\sqrt{a_1a_2a_3}$ used in equation (148).

with the condition that

$$\int \phi^2 d\tau = \int \phi^2 \sqrt{A}\, dq_i \ldots . dq_f = 1, \qquad (369)$$

where the integration is carried out over the whole configuration space.

Now in any treatise on the calculus of variation it is shown that, given a definite integral of the form

$$I = \int F\left(q_i, \phi, \frac{\partial \phi}{\partial q_i}\right) d\tau,$$

the condition to be satisfied in order that this integral shall be a minimum is given by the Euler equation,

$$\sum_i \frac{\partial}{\partial q_i}\left(\frac{\partial F}{\partial \phi_i}\right) - \frac{\partial F}{\partial \phi} = 0 \qquad (370)$$

where $\phi_j = \dfrac{\partial \phi}{\partial q_j}$, and i and j are any pair of the numbers $1, 2 \ldots f$.

If we apply this condition to the integral in (368) we obtain the S. equation

$$\frac{h^2}{4\pi^2} \frac{1}{\sqrt{A}} \sum_i \frac{\partial}{\partial q_i}\left(\sqrt{A} \sum_k A_{ik} \frac{\partial \phi}{\partial q_k}\right) + (E^0 - V)\phi = 0, \qquad (371)$$

where E^0 is the minimum value of I in (368) for a given form of ϕ, and A_{ik} is a coefficient of the term involving $\partial^2\phi/(\partial q_i \partial q_k)$.

Thus equation (370) leads to the expression for the Laplacian operator in the S. equation,*

$$\frac{h^2}{8\pi^2\mu} \nabla^2\phi + (E - V)\phi = 0$$

As an illustration of the application of these equations, let us consider the problem of the linear harmonic oscillator, which was discussed in Chapter IV.

In terms of q, the displacement, and p, the corresponding momentum,

$$E = H(p, q) = \frac{p^2}{2\mu} + \frac{kq^2}{2}$$

Hence, the variational function is given by

$$I = \int_{-\infty}^{\infty} \left\{\frac{h^2}{8\pi^2\mu}\left(\frac{\partial \phi}{\partial q}\right)^2 + \frac{kq^2\phi^2}{2}\right\} dq = \text{minimum} = E,$$

with the condition $\displaystyle\int_{-\infty}^{\infty} \phi^2 dq = 1.$

We can combine these two relations in the form, analogous to equation (366) or (371),

$$\delta(I - E) = \delta \int_{-\infty}^{\infty} \left\{\frac{h^2}{8\pi^2\mu}\left(\frac{d\phi}{dq}\right)^2 + \frac{kq^2\phi^2}{2} - E\phi^2\right\} dq = 0.$$

Denoting the expression in the integrand by $F(q, \phi, d\phi/dq)$, it is evident, if we denote $d\phi/dq$ by ϕ_q, that

$$\frac{\partial F}{\partial \phi_q} = \frac{2h^2}{8\pi^2\mu} \cdot \frac{d\phi}{dq}$$

so that

$$\frac{d}{dq}\left(\frac{\partial F}{\partial \phi_q}\right) = \frac{2h^2}{8\pi^2\mu} \cdot \frac{d^2\phi}{dq^2}$$

while

$$\frac{\partial F}{\partial \phi} = 2\left(\frac{kq^2}{2} - E\right)\phi$$

Hence

$$\frac{d}{dq}\left(\frac{\partial F}{\partial \phi_q}\right) - \frac{\partial F}{\partial \phi} = \frac{2h^2}{8\pi^2\mu} \cdot \frac{d^2\phi}{dq^2} + 2\left(E - \frac{kq^2}{2}\right)\phi$$
$$= 0 \text{ if } (I - E) \text{ is to be a minimum.}$$

The right-hand expression in the last equation is obviously the same as the S. equation (108a) of Chapter IV.

APPLICATION TO NORMAL STATE OF THE HELIUM ATOM

In Part I of this chapter the energy of the normal state of the helium atom was calculated by use of the first-order perturbation theory. It will now be shown that by use of the variational method it is possible to approach the correct value of E much more closely.†

The S. equation for the system in terms of atomic units, as derived previously, is

$$\nabla_1^2\phi + \nabla_2^2\phi + \left(\lambda + \frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{2}{Z\rho_{12}}\right)\phi = 0 \qquad (327)$$

Let us assume the existence of a solution of the form,

$$\phi_0 = \phi(\rho_1)\phi(\rho_2) = \frac{\epsilon^{-\beta(\rho_1 + \rho_2)}}{N} \qquad (372)$$

where N is the normalizing factor, and β, a parameter which has to be determined from the relation,

$$\partial\lambda/\partial\beta = 0$$

This equation merely indicates that the value of β must be chosen to satisfy the requirement that it shall lead to a minimum value of the energy, λ (or E).

The value of N in equation (372) is derived as follows:

$$1 = \int_{\rho_1=0}^{\infty} \int_{\rho_2=0}^{\infty} \phi_0^2 \cdot 4\pi\rho_1^2 \cdot 4\pi\rho_2^2 d\rho_1 d\rho_2$$
$$= \frac{16\pi^2}{N^2} \int \epsilon^{-2\beta(\rho_1 + \rho_2)} \rho_1^2 \rho_2^2 d\rho_1 d\rho_2$$
$$= \frac{16\pi^2}{N^2} \left\{\int_0^{\infty} \epsilon^{-2\beta\rho} \rho^2 d\rho\right\}^2$$
$$= \frac{16\pi^2}{N^2} \left\{\int_0^{\infty} \epsilon^{-x} x^2 dx\right\}^2 \left(\frac{1}{8\beta^3}\right)^2$$

where $x = 2\beta\rho$

But

$$\int_0^{\infty} \epsilon^{-x} x^2 dx = 2$$

* See also E. U. CONDON AND P. M. MORSE, "Quantum mechanics," Chapter I, and E. C. KEMBLE, *Phys. Rev. Supplement*, **1**, 157 (1929), for more detailed discussion of this topic.

† The calculation discussed in the following section was first given by J. FRENKEL, "Einführung in die Wellenmechanik," Julius Springer, **1929**, pp. 291–3. (It has also been given in a modified form by C. ECKART, *loc. cit.*, and by PAULING AND WILSON, "Introduction to quantum mechanics," pp. 184–5.)

Hence $N = \pi/\beta^3$, and the normalized function is

$$\phi_0 = \phi(\rho_1)\phi(\rho_2) = \frac{\beta^3}{\pi} \cdot \epsilon^{-\beta(\rho_1 + \rho_2)} \tag{373}$$

The significance of β is readily evident from a consideration of the wave equation

$$\nabla^2\phi - \left(\beta^2 - \frac{2\beta}{\rho}\right)\phi = 0 \tag{374}$$

The normalized solution of this equation is

$$\phi(\rho) = -\sqrt{\beta^3/\pi} \cdot \epsilon^{-\beta\rho}$$

with the eigenvalue,

$$E^0 = -\beta^2 \cdot RchZ^2$$

Equation (374) is therefore similar to equation (325*b*) of Part I, and represents the S. equation for a hydrogen-like atom of "effective" nuclear charge $\beta \cdot Ze$, where Ze is the true nuclear charge. Thus the suggestion of a solution for the helium atom of the form indicated in equation (373) may be interpreted thus:

We regard the repulsive interaction of the electrons as equivalent in effect to a decreased force of attraction between each electron and the nucleus. That is, instead of regarding each electron as acted upon by a nuclear charge of magnitude Ze, we replace the latter by an effective charge of magnitude $\beta \cdot Ze$, where $\beta < 1$. From this point of view we may also consider that each electron screens the other electron to some extent and hence we may designate $(1 - \beta)$ as the "screening constant."*

Now the application of the variational method, as discussed in the previous section, leads in the case of equation (327) to the requirement that

$$I = \int \phi_0 H \phi_0 d\tau = \text{minimum} = E^0 \tag{375}$$

where $d\tau = 4\pi\rho_1^2 d\rho_1 \cdot 4\pi\rho_2^2 d\rho_2$, and the limits of integration for ρ_1 and ρ_2 are 0 to ∞, while

$$H = -\left(\nabla_1^2 + \nabla_2^2 + \frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{2}{Z\rho_{12}}\right) \tag{376}$$

and ϕ_0 is defined by equation (373).
Hence

$$H\phi_0 = -[\phi(\rho_2)\nabla^2\phi(\rho_1) + \phi(\rho_1)\nabla^2\phi(\rho_2)] - \left(\frac{2}{\rho_1} + \frac{2}{\rho_2} - \frac{2}{Z\rho_{12}}\right)\phi(\rho_1)\phi(\rho_2)$$

But from equation (374) it is seen that

$$\nabla^2\phi(\rho_1) = \left(\beta^2 - \frac{2\beta}{\rho_1}\right)\phi(\rho_1)$$

and similarly for $\phi(\rho_2)$.

Therefore

$$\phi_0 H \phi_0 = \{\phi(\rho_1)\phi(\rho_2)\}^2 \left\{-2\beta^2 + \frac{2\beta}{\rho_1} + \frac{2\beta}{\rho_2} - \frac{2}{\rho_1} - \frac{2}{\rho_2} + \frac{2}{Z\rho_{12}}\right\}$$

and

$$I = J_1 + J_2 + J_3$$

where

$$J_1 = -32\beta^3 \int_0^\infty \epsilon^{-2\beta(\rho_1 + \rho_2)} \rho_1^2 \rho_2^2 d\rho_1 d\rho_2$$

$$J_2 = 32\beta^6(\beta - 1) \int_0^\infty \epsilon^{-2\beta(\rho_1 + \rho_2)} \left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) \rho_1^2 \rho_2^2 d\rho_1 d\rho_2$$

and

$$J_3 = \frac{32\beta^6}{Z} \int_0^\infty \epsilon^{-2\beta(\rho_1 + \rho_2)} (1/\rho_{12}) \rho_1^2 \rho_2^2 d\rho_1 d\rho_2$$

The evaluation of these integrals is as follows:

$$J_1 = -32\beta^3 \left\{\int \epsilon^{-2\beta\rho} \rho^2 d\rho\right\}^2 = -2\beta^2$$

$$J_2 = 32\beta^6(\beta - 1) \cdot 2 \int \epsilon^{-2\beta(\rho_1 + \rho_2)} \rho_1 \rho_2^2 d\rho_1 d\rho_2$$

which results from the fact that the integral is symmetrical with respect to ρ_1 and ρ_2. Hence

$$J_2 = 64\beta^6(\beta - 1) \int \epsilon^{-2\beta\rho} d\rho \int \epsilon^{-2\beta\rho} \rho^2 d\rho = 4\beta(\beta - 1)$$

while

$$J_3 = \frac{32\beta^6}{Z\beta^5} \int \frac{\epsilon^{-2(x_1 + x_2)}}{x_{12}} x_1^2 x_2^2 dx_1 dx_2$$

where $x_1 = \beta\rho_1$; $x_2 = \beta\rho_2$; $x_{12} = \beta\rho_{12}$.

This integral was evaluated in the previous chapter, and substituting from equation (336) it follows that:

$$J_3 = \frac{32\beta}{Z} \cdot \frac{5}{128} = \frac{5\beta}{8}, \text{ since } Z = 2, \text{ for helium.}$$

Consequently,

$$\begin{aligned} E^0 &= J_1 + J_2 + J_3 \\ &= -2\beta^2 + 4\beta(\beta - 1) + (5/8)\beta \\ &= 2\left(\beta^2 - \frac{27\beta}{16}\right) \end{aligned}$$

and

$$\frac{dE^0}{d\beta} = 2(2\beta - 27/16)$$

The condition $dE^0/d\beta = 0$ leads to the result

$$\beta = 27/32$$

from which it follows that

$$\begin{aligned} E^0 &= 2\beta(\beta - 27/16) \cdot RchZ^2 \\ &= -\frac{729}{512} \cdot RchZ^2. \end{aligned}$$

This represents the energy of formation of He from the two electrons and a nucleus of charge Ze. Hence, the ionization energy of the helium atom is given by

$$E_i = \left(-\frac{729}{512} + 1\right) RchZ^2$$

and

$$\begin{aligned} V_i &= \text{ionization potential} \\ &= \frac{217}{512} \times 4 \times 13.54 \text{ volts} \\ &= 22.96 \text{ volts.} \end{aligned}$$

It will be observed that this value is 1.50 volts less than the observed value (24.46 volts), whereas the

* See C. ECKART, *loc. cit.*

first-order perturbation relation leads to a discrepancy of 4.12 volts.

The value $\beta = 27/32$ means that the effective nuclear charge is 27/16 in units of e (the charge on the electron), and that consequently the interaction of the electrons is equivalent to a decrease of $^5/_{16}$ units in the nuclear charge.

Instead of the form assumed for the function ϕ_0 in the preceding discussion it is obviously possible to find other forms which lead to minima that approach the true value more closely. A number of theoretical physicists have attacked this problem by more involved mathematical methods,* and of these the most successful results have been obtained by E. A. Hylleraas.†

The method used by the latter involves the choice of a type of coördinate which has also proved suitable for other kinds of problems in quantum mechanics. For this reason a summary is given in the following section of the technic used by Hylleraas.

VARIATIONAL METHOD OF HYLLERAAS‡

Instead of spherical polar coördinates, Hylleraas uses the coördinates r_1, r_2, and r_{12} which correspond to the three sides of the triangle formed by the nucleus and the two electrons. In terms of these coördinates the element of volume is derived as follows. Let r_1, η, ζ denote the polar coördinates of the first electron, and r_2, θ, χ, those of the second referred to the vector r_1 as polar axis. The angle between r_1 and r_2 is given by θ, and hence

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\theta$$

so that

$$r_{12}dr_{12} = r_1r_2\sin\theta d\theta$$

The element of volume is given by

$$d\tau' = r_2^2\sin\theta\, dr_2d\theta d\chi\cdot r_1^2\sin\eta\, dr_1d\eta d\zeta$$
$$= r_1r_2r_{12}dr_1dr_2dr_{12}d\chi\cdot\sin\eta\, d\eta d\zeta$$

For spherically symmetrical distributions, we may replace $d\tau'$ by the element of volume,

$$d\tau = r_1r_2r_{12}dr_1dr_2dr_{12}\int_0^\pi\sin\eta\, d\eta\int_0^{2\pi}d\chi\int_0^{2\pi}d\zeta$$
$$= 8\pi^2\cdot r_1r_2r_{12}dr_1dr_2dr_{12}$$

Now let us introduce the so-called "elliptical" coördinates,

$$s = r_1 + r_2 \qquad (377)$$

$$t = r_1 - r_2 \qquad (378)$$

and let

$$u = r_{12} \qquad (379)$$

Since $4r_1r_2 = s^2 - t^2$,

$$d\tau = 2\pi^2(s^2 - t^2)u\cdot du\cdot dr_1dr_2 \qquad (380)$$

In order to express the element of area dr_1dr_2 in terms of $ds\cdot dt$ we make use of the following relation between these elements (which is derived in any treatise on integral calculus).**

$$\left(\frac{\partial t}{\partial r_1}\cdot\frac{\partial s}{\partial r_2} - \frac{\partial t}{\partial r_2}\cdot\frac{\partial s}{\partial r_1}\right)dr_1dr_2 = ds\cdot dt \qquad (i)$$

From the functional relations between s, t, r_1, and r_2 in equations (377) and (378) it is evident that

$$\frac{\partial s}{\partial r_1} = 1;\quad \frac{\partial t}{\partial r_1} = 1;\quad \frac{\partial s}{\partial r_2} = 1;\quad \frac{\partial t}{\partial r_2} = -1 \qquad (ii)$$

Consequently (i) becomes

$$2dr_1dr_2 = ds\cdot dt \qquad (iii)$$

and (380) becomes

$$d\tau = \pi^2(s^2 - t^2)u\cdot du\cdot ds\cdot dt \qquad (381)$$

The limits of integration are evidently,

$$-u \leqq t \leqq u,$$
$$0 \leqq u \leqq s \leqq \infty$$

Let $\phi(s, t, u)$ denote some function of the coördinates such that

$$I = \frac{1}{N}\int\phi H\phi d\tau = \text{minimum} = E$$

subject to the condition

$$N = \int\phi^2 d\tau$$

In terms of atomic units, it follows from (376) that

$$\phi H\phi = -\phi\{\nabla_1^2\phi + \nabla_2^2\phi - V\phi\} \qquad (382)$$

where V is the potential energy expressed as a function of r_1, r_2, and r_{12}.

By application of Green's theorem it is possible to transform equation (382) into a more suitable form. In treatises on integral calculus or on electricity and magnetism††† it is shown that if U is a function of the rectangular coördinates x, y, z, then

$$\int\int\int U\nabla^2U dxdydz + \int\int\int\left\{\left(\frac{\partial U}{\partial x}\right)^2 + \left(\frac{\partial U}{\partial y}\right)^2 + \left(\frac{\partial U}{\partial z}\right)^2\right\} dxdydz + \int\int U\frac{\partial U}{\partial n}ds = 0 \qquad (383)$$

where $\partial U/\partial n$ is the rate of change of U along the normal at any point on a surface described in the configuration space, and ds is an element of area on this surface. If the integration indicated in the first two integrals is carried out over the whole configuration space (that is, with the limits $x = y = z = \pm\infty$), the values of U and $\partial U/\partial n$ on the surface described at these limits must vanish, if U is a solution of the S. equation. Also the integrand in the second term of this equation is evidently equal to $(\partial U/\partial n)^2$, that is, to the square of the gradient along the diagonal of the element of volume $dxdydz$. Hence, we can express equation (383) in the form

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* A list of the variational functions used and of the values of E calculated by each of these methods is given by L. PAULING AND E. B. WILSON, "Introduction to quantum mechanics," p. 224.

† E. A. HYLLERAAS, *Z. Physik*, **48**, 469 (1928); **54**, 347 (1929); **65**, 209 (1930).

‡ In connection with the topic of this section, the reader will find an extremely illuminating discussion by H. BETHE, "Handbuch der Physik," **XXIV**, Part 1, pp. 354–5, Julius Springer, Berlin, 1933.

** The expression in the brackets is known as a Jacobian.

††† For example, J. H. JEANS, "Electricity and magnetism."

$$\int U\nabla^2 U dxdydz = -\int (\text{grad. } U)^2 dxdydz \qquad (384)$$

where the limits of integration are $x = y = z = \pm\infty$.

In the case of the function $\phi(r_1, r_2, r_{12})$,

$$r_1^2 = x_1^2 + y_1^2 + z_1^2$$
$$r_2^2 = x_2^2 + y_2^2 + z_2^2$$

and

$$r_{12}^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2$$

where $x_1y_1z_1$ are the coördinates of the first electron and $x_2y_2z_2$ refer to the second electron.

Now

$$\frac{\partial\phi}{\partial x_1} = \frac{\partial\phi}{\partial r_1}\cdot\left(\frac{\partial r_1}{\partial x_1}\right) + \frac{\partial\phi}{\partial r_{12}}\cdot\frac{\partial r_{12}}{\partial x_1}$$
$$= \frac{\partial\phi}{\partial r_1}\cdot\frac{x_1}{r_1} + \frac{\partial\phi}{\partial r_{12}}\cdot\frac{x_1 - x_2}{r_{12}}$$

Hence, for the first electron

$$(\text{grad.}_1\,\phi)^2 = \left(\frac{\partial\phi}{\partial x_1}\right)^2 + \left(\frac{\partial\phi}{\partial y_1}\right)^2 + \left(\frac{\partial\phi}{\partial z_1}\right)^2$$
$$= \left(\frac{\partial\phi}{\partial r_1}\right)^2 + \left(\frac{\partial\phi}{\partial r_{12}}\right)^2 + \frac{\partial\phi}{\partial r_1}\cdot\frac{\partial\phi}{\partial r_{12}}\left\{\frac{2x_1(x_1 - x_2)}{r_1r_{12}} + \frac{2y_1(y_1 - y_2) + 2z_1(z_1 - z_2)}{r_1r_{12}}\right\}$$
$$= \left(\frac{\partial\phi}{\partial r_1}\right)^2 + \left(\frac{\partial\phi}{\partial r_{12}}\right)^2 + \frac{\partial\phi}{\partial r_1}\cdot\frac{\partial\phi}{\partial r_{12}}\cdot\frac{r_1^2 + r_{12}^2 - r_2^2}{r_1r_{12}}$$

and a similar expression may be derived for $(\text{grad.}_2\,\phi)^2$, which refers to the second electron.

In terms of the variables s, t, u,

$$\frac{\partial\phi}{\partial r_1} = \frac{\partial\phi}{\partial s}\cdot\frac{\partial s}{\partial r_1} + \frac{\partial\phi}{\partial t}\cdot\frac{\partial t}{\partial r_1} = \frac{\partial\phi}{\partial s} + \frac{\partial\phi}{\partial t}$$
$$\frac{\partial\phi}{\partial r_2} = \frac{\partial\phi}{\partial s} - \frac{\partial\phi}{\partial t}$$
$$\frac{\partial\phi}{\partial r_{12}} = \frac{\partial\phi}{\partial u}$$

Hence

$$(\text{grad.}_1\,\phi)^2 + (\text{grad.}_2\,\phi)^2 = 2\left(\frac{\partial\phi}{\partial s}\right)^2 + 2\left(\frac{\partial\phi}{\partial t}\right)^2 + 2\left(\frac{\partial\phi}{\partial u}\right)^2 + \frac{4}{u(s^2 - t^2)}\cdot\frac{\partial\phi}{\partial u}\left[s(u^2 - t^2)\frac{\partial\phi}{\partial s} + t(s^2 - u^2)\frac{\partial\phi}{\partial t}\right] \qquad (385)$$

Thus the integral to be minimized is

$$I = \frac{\int\phi H\phi d\tau}{\int\phi^2 d\tau} = \frac{\int\{(\text{grad.}_1\,\phi)^2 + (\text{grad.}_2\,\phi)^2\}\phi d\tau}{\int\phi^2 d\tau} + \frac{\int V\phi^2 d\tau}{\int\phi^2 d\tau} \qquad (386)$$

The potential energy function is

$$V = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{Zr_{12}} = -\frac{8s}{s^2 - t^2} + \frac{2}{Zu}$$
$$= -\frac{2(4Zus - s^2 + t^2)}{Zu(s^2 - t^2)} \qquad (387)$$

From equations (385), (386), and (387) it follows that the integral to be minimized has the form

$$I = \frac{M - L}{N} = E \qquad (388)$$

where

$$M = Z\int_0^\infty ds\int_0^s du\int_0^u dt\left\{u(s^2 - t^2)\left[\left(\frac{\partial\phi}{\partial s}\right)^2 + \left(\frac{\partial\phi}{\partial t}\right)^2 + \left(\frac{\partial\phi}{\partial u}\right)^2\right] + \frac{2\partial\phi}{\partial u}\left[s(u^2 - t^2)\frac{\partial\phi}{\partial s} + t(s^2 - u^2)\frac{\partial\phi}{\partial t}\right]\right\} \qquad (389)$$

$$L = \int_0^\infty ds\int_0^s du\int_0^u dt\,\phi^2(4Zus - s^2 + t^2) \qquad (390)$$

$$N = \int_0^\infty ds\int_0^s du\int_0^u dt\,u(s^2 - t^2)\phi^2 \qquad (391)$$

Owing to the fact that $\phi^2(s, t, u) = \phi^2(s, -t, u)$, and $\phi H\phi(s, t, u) = \phi H\phi(s, -t, u)$, the limits of integration have been taken as $0 \leqq t \leqq u \leqq s \leqq \infty$, and this leads to the elimination of the factor 2 in the expressions for M, L, and N.

Equation (388) may be written in the form

$$\delta(M - L - NE) = 0 \qquad (392)$$

indicating that the expression in the brackets is to be a minimum.

We now have to consider different forms of the expression for ϕ, and the simplest form is that chosen in the previous section, *viz.*:

$$\phi = \epsilon^{-k(r_1 + r_2)} = \epsilon^{-ks} \qquad (393)$$

where, for the present, the normalization factor may be omitted, and k is a parameter, the value of which has to be determined from the condition (392).

Since

$$\int_0^\infty ds\int_0^s du\int_0^u dt(s^2 - t^2) = \int_0^\infty ds\int_0^s du\cdot u\left(s^2u - \frac{u^3}{3}\right)$$
$$= \int_0^\infty ds\left(\frac{s^5}{3} - \frac{s^5}{15}\right) = \int_0^\infty ds\cdot\frac{4}{15}s^5$$

while

$$\int_0^\infty ds\int_0^s du\int_0^u dt(4Zus - s^2 + t^2)$$
$$= \int_0^\infty ds\int_0^s du\left\{(4Zus - s^2)u + \frac{u^3}{3}\right\}$$
$$= \int_0^\infty ds\left\{\frac{4Z}{3} - \frac{5}{12}\right\}s^4$$

and

$$\frac{\partial\phi}{\partial t} = \frac{\partial\phi}{\partial u} = 0,$$

equation (388) or (392) reduces to

$$\delta\int_0^\infty ds\left\{\frac{4Zs^5}{15}\left(\frac{d\phi}{ds}\right)^2 - \left(\frac{4Z}{3} - \frac{5}{12}\right)s^4\phi^2 - \frac{4Es^5}{15}\phi^2\right\} = 0 \qquad (394)$$

The Euler equation which this variation problem must satisfy is

$$\frac{d}{ds}\cdot\frac{\partial F}{\partial(d\phi/ds)} - \frac{\partial F}{\partial\phi} = 0 \qquad (395)$$

where F denotes the function in the large brackets of equation (394).

Since

$$\partial F/\partial(d\phi/ds) = \frac{8Zs^5}{15}\cdot\frac{d\phi}{ds}$$

and

$$\frac{\partial F}{\partial \phi} = 2s^4\left(\frac{4Z}{3} - \frac{5}{12} - \frac{4Es}{15}\right)\phi,$$

therefore the Euler condition (395) corresponds to the differential equation,

$$\frac{8Zs^5}{15}\frac{d^2\phi}{ds^2} + \frac{8Zs^4}{3}\cdot\frac{d\phi}{ds} - 2s^4\left(\frac{4Z}{3} - \frac{5}{12} - \frac{4Es}{15}\right)\phi$$

that is,

$$\frac{d^2\phi}{ds^2} + \frac{5}{s}\cdot\frac{d\phi}{ds} + \left(\frac{E}{Z} + \frac{5}{s} - \frac{25}{16Zs}\right)\phi = 0$$

which is the corresponding S. equation.

Substituting for ϕ from equation (393), the result is

$$k^2 - \frac{5k}{s} + \frac{E}{Z} + \frac{5}{s} - \frac{25}{16Zs} = 0$$

Since this relation must be valid for all values of s we must have the following two relations:

$$k = 1 - \frac{5}{16Z} = \frac{27}{32}$$

which arises from equating to zero the terms involving s, and

$$\frac{E}{Z} = -k^2 = \left(1 - \frac{5}{16Z}\right)^2$$

That is,

$$E = -2\left(\frac{27}{32}\right)^2\cdot RchZ^2$$

$$= -\frac{729}{512}\cdot RchZ^2$$

and

$$\phi = \epsilon^{-27/32}$$

It will be observed that except for the normalization factor, this is the same solution as that obtained previously. If we wish to express ϕ as a function of s alone, the method used in the first part of this chapter is obviously much more convenient. However, the advantage of Hylleraas' method is that we can substitute for ϕ in equation (388) such a complicated expression as

$$\phi(s, t, u) = \epsilon^{-s/2}P(s, t, u)$$

where

$$P = \sum_{n,l,m} A_{n,2l,m}s^n t^{2l}u^m$$

that is, where ϕ is expressed as a *series* of terms in powers of s, t, and u. Under these conditions it is necessary to solve a number of simultaneous equations of the form

$$\frac{\partial E}{\partial A_{n,2l,m}} = 0$$

and the calculation becomes extremely lengthy. However, Hylleraas has succeeded in this manner in deriving a value for the ionization potential of helium which differs from the observed value by only -0.0016 electron volt.

THE PROBLEM OF THE MANY-ELECTRON ATOM

The discussion in the previous sections indicates that even in the case of the two-electron system, the problem of solving the S. equation involves a great deal of tedious calculation, if results of any considerable degree of accuracy are required. It is obvious that the difficulties encountered in solving the corresponding equation in the case of the many-electron atom must be even greater. In the following section some of the more outstanding methods which have been developed for the solution of this quite complex problem are described quite briefly. The reader who desires to follow up this aspect of quantum mechanics will find more complete details in the references which accompany the discussion.*

The wave equation for an atom with N electrons, and a nuclear charge, $+Ze$, is evidently

$$\sum_{i=1}^{N}\nabla_i^2\phi + \frac{8\pi^2\mu}{h^2}\left(E + \sum_{i=1}^{N}\frac{Ze^2}{r_i} - \sum\frac{e^2}{r_{ij}}\right)\phi = 0 \quad (396)$$

where r_i is the distance of the ith electron from the nucleus, and r_{ij} is the distance between the ith and jth electrons. In the last summation, the number of terms must be the same as the number of combinations of N things, when taken two at a time, which is equal to

$$C_2(N) = \frac{N!}{(N-2)!\,2!}$$

In terms of atomic units, equation (396) has the form,

$$\sum_{i=1}^{N}\nabla_i^2\phi + 2\left(\frac{\lambda}{2} + \sum_{i=1}^{N}\frac{1}{\rho_i} - \frac{1}{Z}\sum\frac{1}{\rho_{ij}}\right)\phi = 0 \quad (397)$$

which, as is evident, becomes identical with equation (327) for $N = 2$. If the "perturbation" terms in ρ_{ij} were absent, the solution would be the product of N eigenfunctions, one for each electron. As in the case of the excited states of the helium atom, it is, however, possible for electrons to interchange quantum numbers and consequently the problem is usually degenerate.

J. C. Slater† has shown that the only possible "zero order" function which is *antisymmetric* and will satisfy the Pauli exclusion principle is the function represented by the determinant,

$$\phi^0 = \frac{1}{\sqrt{N}}\begin{vmatrix} u(n_1/x_1), & u(n_1/x_2) & \cdots & u(n_1/x_N) \\ u(n_2/x_1), & u(n_2/x_2) & \cdots & u(n_2/x_N) \\ \cdots & \cdots & \cdots & \cdots \\ u(n_N/x_1), & u(n_N/x_2) & \cdots & u(n_N/x_N) \end{vmatrix} \quad (398)$$

where $u(n_i/x_j)$ represents the *single electron eigenfunction* for the ith electron, n_i stands for the four quantum numbers, n_i, l_i, m_i, and $(m_s)_i$, and x_j symbolizes the four coördinates (three of position, and one of spin). Thus, $u(n_2/x_1)$ and $u(n_1/x_2)$ are obtained from $u(n_1/x_1)$ and $u(n_2/x_2)$ by interchanging the coordinates of electrons 1 and 2.

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* The reader should consult the comprehensive discussion of this topic by L. A. PAULING AND E. B. WILSON, JR., "Introduction to quantum mechanics," Chapter IX.

† J. C. SLATER, *Phys. Rev.*, **34**, 1293 (1929).

In the calculation of the perturbation energy due to the terms containing ρ_{ij}, a secular equation has to be solved which is of degree N and is of the form shown in equation (311). This involves the solution of two types of integrals which have been designated by Slater and other writers as of types J and K, respectively. Type J is of the same nature as H_{11} in equation (346), so that J_{ij} represents the *Coulomb interaction* of the ith and jth electrons, while K_{ij} is an *exchange energy* term corresponding to H_{12} in equation (347).

The application of the perturbation theory to this problem has also been discussed by J. E. Lennard-Jones.* On the other hand, V. Fock† and other investigators have obtained results of a high degree of accuracy by application of the variational method.

Finally, it is of interest to describe briefly a method for calculating the distribution functions of electrons in complex atoms which has been developed and utilized very successfully by D. R. Hartree‡ and his associates. This method is essentially a scheme for replacing the perturbation terms involving Coulomb interaction between pairs of electrons, by non-Coulomb potential functions for each electron, with the result that the S. equation can be solved as the product of two or more single-electron wave functions. The method may be described best by considering its application in the case of helium atom.**

Let us assume that the potential energy function can be represented as the sum of two terms in the form

$$V = V_1(\rho_1) + V_2(\rho_2)$$

where V_1 is a function of ρ_1, θ_1, and η_1, the coördinates of one electron, and V_2 represents another function for the other electron. From a knowledge of these functions it should be possible to represent the eigenfunction for the system as the product of two functions, $\phi_1(\rho_1)$ and $\phi_2(\rho_2)$. But in that case, the potential field acting on electron 1 is given by

$$V_1(\rho_1) = -\frac{Z_1}{\rho_1} + \int \phi_2^2(\rho_2)\,\frac{d\tau_2}{\rho_{12}} \qquad (399)$$

where the first term represents the attraction due to the nucleus, and the second term, the repulsion due to the *averaged* charge distribution produced by the motion of the second electron.

Thus, if we can make a good guess regarding the actual form of $\phi_2(\rho_2)$, it is possible to calculate $V_1(\rho_1)$ and this should satisfy the S. equation for electron 1 in the form,

$$\nabla^2\phi_1(\rho_1) + [E_1 - V_1(\rho_1)]\phi_1(\rho_1) = 0 \qquad (400)$$

The solution of this equation gives $\phi_1(\rho_1)$ and consequently leads, by an equation similar to (399), to an expression for $V_2(\rho_2)$, which gives the average potential field in which electron 2 moves. Therefore, we can now solve an equation similar to (400) for $\phi_2(\rho_2)$. The form of the function thus obtained should agree with that assumed in solving equation (399). This is the explanation for the designation of Hartree's method as that of "*the self-consistent field.*"

Obviously, this method of "trial and error" can be repeated until the desired degree of agreement is obtained between the form of the potential function $V_1(\rho_1)$ assumed initially and that derived from the final step in the argument.

It will be observed that the use of this scheme avoids the necessity for calculating exchange terms as in the application of the other methods. But in a sense Hartree's method may be regarded as one in which the effect on the calculated value of E, which results from a variation in the form of $\phi(\rho)$, is determined. Thus the method of the self-consistent field differs from the variational method as used by Hylleraas in this respect, that while the latter investigates the effect on a given wave function of varying one or more arbitrary parameters, Hartree's method involves an investigation of the effect of varying the nature of the wave function itself. J. C. Slater††† has examined Hartree's method critically as to its accuracy as a method of solving the S. equation and has pointed out the conditions under which the solutions and energy values thus obtained might deviate to a considerable extent from the correct values. However, Slater has also shown*** that in the case of normal helium the method yields an electron distribution function which agrees well with that found independently by Hartree and an ionization energy which is within 1% of the observed value. Furthermore, Hartree and his associates have applied the method to calculate distribution functions for electrons in more complex atoms and have obtained results which are in substantial agreement with deductions from observations on the scattering of X-rays and electrons by atoms.

* J. E. LENNARD-JONES, *Proc. Roy. Soc.*, **A129**, 598 (1930), and *Proc. Cambridge Phil. Soc.*, **27**, 469 (1931).

† V. FOCK, *Z. Physik*, **61**, 126 (1930).

‡ D. R. HARTREE, *Proc. Cambridge Phil. Soc.*, **24**, 89, 111, 426 (1928) and subsequent papers in *Proc. Roy. Soc.*, **A**.

** This illustration is given by N. F. MOTT, "Wave mechanics," p. 120. See also H. BETHE's discussion, "Handbuch der Physik," XXIV, Part I, pp. 327–8, 368–70, Julius Springer, Berlin, **1933**, and L. A. PAULING AND E. B. WILSON, *loc. cit.*

*** J. C. SLATER, *Phys. Rev.*, **32**, 339 (1928).

††† J. C. SLATER, *ibid.*, **32**, 349 (1928).

FIRE AT THE UNIVERSITY OF PITTSBURGH

The laboratories which were employed for instruction in the first-year inorganic and organic chemistry courses in the University of Pittsburgh took fire on Thursday, January 16th, and were completely demolished. New laboratories, completely equipped, were ready for occupancy by the students on Thursday, February 6th. About five hundred students are enrolled in these courses.

ISOPIESTIC METHOD *for the* DETERMINATION *of* MOLECULAR WEIGHTS

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A simple apparatus for the measurement of the relative vapor pressure of aqueous solutions is described. An experiment for the determination of molecular weights from the vapor-pressure lowering is outlined. This experiment is shown to be suitable for students in the elementary physical chemistry laboratory.

✦ ✦ ✦ ✦ ✦ ✦

EXCEPT for the none too satisfactory apparatus of Menzies (*1*) there seems to be no practical method for the determination of molecular weights from vapor-pressure lowering in the elementary physical chemistry laboratory.

In the present experiment the vapor pressure of a solution is measured in terms of the vapor pressure of a standard solution.

Samples of the solution are placed in a closed container with samples of the standard solution. When equilibrium is attained the vapor pressure of the solution will be the same as that of the standard. The molecular weight is then calculated from the vapor-pressure lowering as determined from the vapor pressure of the unknown solution.

THEORY INVOLVED

It is a well-known fact that if the vapor pressure of a solution could be determined, the molecular weight of the dissolved substance could easily be calculated. From Raoult's Law we have:

$$\frac{p_0 - p}{p_0} = x = \frac{\frac{g}{m}}{\frac{G}{M} + \frac{g}{m}}, \qquad (1)$$

where x = mol fraction of solute,
g = weight of solute present,
G = weight of solvent present,
m = molecular weight of the dissolved solute,
M = molecular weight of the solvent,
p_0 = vapor pressure of pure solvent,
p = vapor pressure of solvent in the solution.

We may then write:

$$m = \frac{p_0 g M}{(p_0 - p)G} - g\frac{M}{G} \qquad (2)$$

for the molecular weight of the solute. If we use dilute solutions we may assume the number of moles of solute to be negligible compared to the solvent and write for the molecular weight:

$$m = \frac{gMp_0}{G(p_0 - p)} \qquad (3)$$

APPARATUS

This apparatus is an adaptation of that described by Sinclair (*2*) and used by Robinson and Sinclair (*3*) in their measurement of the activity coefficients of salt solutions.

The apparatus consists essentially of a brass vacuum desiccator as shown in Figures 1 and 2.

The solutions under investigation are weighed into 30-cc. nickel crucibles. These are placed in copper rings soldered to the bottom of the desiccator. This is to prevent them from tipping over. The rings are punched with holes to allow free circulation of the standard solution placed in the bottom of the apparatus. The desiccator is connected through a brass T-tube in the cover to an open-tube mercury manometer not shown in the diagram. The apparatus is evacuated through the T-tube and a shut-off (glass stopcock) by means of a water aspirator.

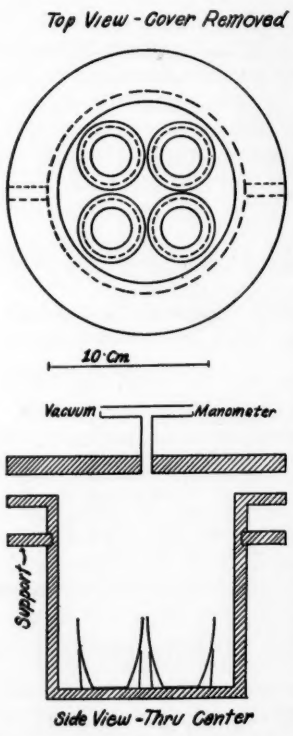

FIGURE 1.—VAPOR-PRESSURE APPARATUS

The apparatus is completely immersed in a water thermostat to prevent condensation of solvent on the cover if the thermostat is above room temperature. The apparatus is suspended in such a manner that it may be rocked or oscillated through a 15° arc about fifty times a minute. This was accomplished by swinging the apparatus in a frame on the round supports indicated in Figure 1. A discarded windshield wiper served very well to operate the apparatus. It was found that a metal apparatus permitted the attaining of equilibrium much more quickly than a glass one.

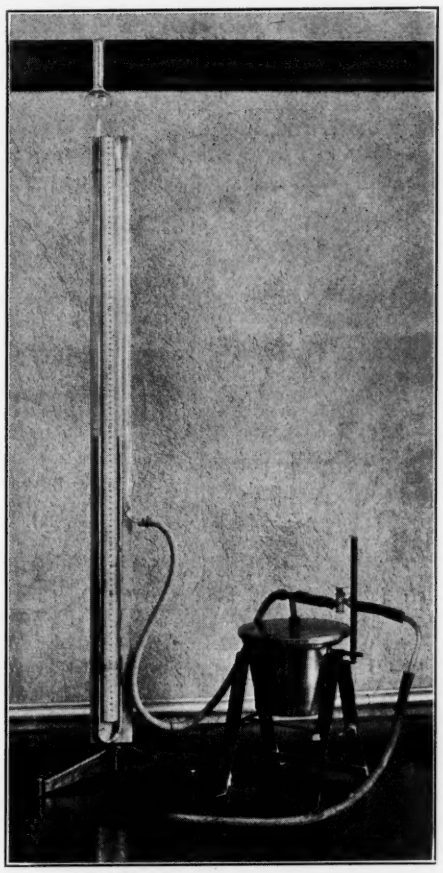

FIGURE 2

EXPERIMENTAL DETAILS

The procedure consists in bringing to the same vapor pressure a standard solution of known vapor pressure and the unknown. For the standard solution we have chosen potassium chloride. The vapor pressures of aqueous solutions of this substance have been carefully determined over a wide range of concentration. Data for these vapor pressures, calculated from recent experimental data (*3*), are given in Table 1 and shown as plotted for use in the calculations in Figure 3.

TABLE 1

THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AT 25°C.

Concentration (moles per 1000 g. solvent)	*Vapor Pressure (mm. of mercury)*
0.1	23.756
0.1	23.677
0.2	23.600
0.3	23.524
0.5	23.374
1.0	22.995
1.5	22.624
2.0	22.243
3.0	21.463
4.0	20.662

The whole procedure is based on the use of about 2 cc. of solution in the crucibles. Enough potassium chloride (0.0746 g.) is weighed into each of two tared nickel crucibles to make approximately 0.5 molal solution with 2 cc. of water.

Enough of the unknown (calculated) is then weighed into each of the other two tared nickel crucibles to give about the same lowering of the vapor pressure as the potassium chloride solutions. Two cc. of water is then added to each crucible and they are placed in the apparatus. A depth of about 1 cm. of 0.5 molal potassium chloride is placed in the bottom of the apparatus to increase the heat transfer and speed up the equilibrium.

The apparatus is then evacuated to about 30 mm. of mercury and the shut-off to the water aspirator is closed. The whole is then placed in the bath and rocked for from 4 to 7 days. A slight rise in pressure on the manometer does no harm as this will not change the partial pressure of water inside the apparatus. If the pressure should rise above 100 mm., equilibrium will not be obtained in the time allowed. At the end of the time specified the apparatus is removed and carefully opened.

The crucibles are placed covered in a desiccator with 0.5 molal potassium chloride in the bottom. This prevents evaporation. They are wiped off with a towel and weighed as rapidly as possible. From the tared weight of the crucible and the salt the weight of water present is easily obtained. The molality of the solution is then calculated from these data. The vapor pressure of a potassium chloride solution of this concentra-

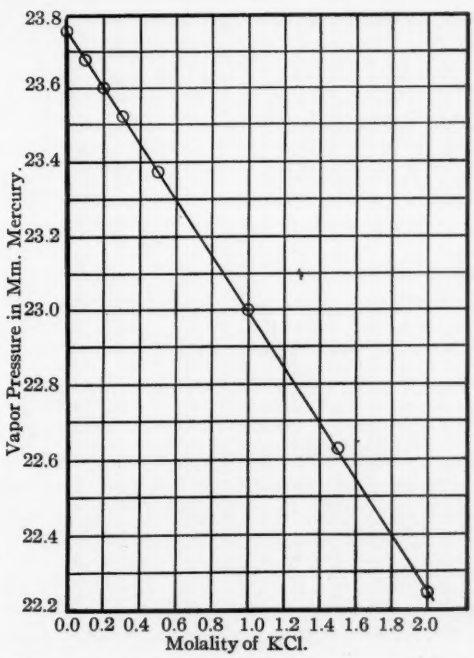

FIGURE 3.—VAPOR PRESSURE OF POTASSIUM CHLORIDE SOLUTIONS

tion is obtained from Table 1. A curve such as is shown in Figure 3 is very useful for this purpose. This gives the vapor pressure of the unknown solution from which its molecular weight is calculated by equation (2).

Table 2 gives a summary of results obtained by students using this apparatus.

TABLE 2

MOLECULAR WEIGHTS OBTAINED BY ISOPIESTIC METHOD

Student	*Substance*	*No. 1*	*No. 2*	*Mean*	*Theoretical*	*% Error*
1	sucrose	339.7	341.6	340.6	342.17	0.42
2	sucrose	337.9	339.3	338.6	342.17	1.04
3	sucrose	342.9	344.2	343.5	342.17	0.38
4	mannitol	182.71	186.37	184.5	182.1	1.31

DISCUSSION

The results obtained, when compared with those usually obtained by elementary students with the cryoscopic and ebullioscopic methods, justify the use of the apparatus described. This apparatus is inexpensive and durable. The time required for performance of the experiment does not exceed two hours.

The authors are indebted to Mr. W. J. Daniels for aid and suggestions in the design of the mechanical equipment and to Mr. G. F. Temple for preparing the drawings.

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STUDENT-TYPE VACUUM-TUBE VOLTMETER

G. F. KINNEY* AND R. L. GARMAN

New York University, Washington Square College, New York

AN INSTRUMENT for general-purpose work or for student use should be rugged, portable, and self-contained. A vacuum-tube voltmeter meeting these requirements is of particular advantage as a measuring instrument for electrometric titrations; in addition to drawing so little current that easily available high-resistance electrodes may be used, it can be made "continuous-reading," and thus the necessity of constantly balancing a potentiometer is eliminated. But vacuum-tube voltmeters are too seldom of the "general-purpose" or "student" type, and the possible conveniences do not always outweigh the trouble necessary to get together, make, and use a vacuum-tube set-up.

A vacuum-tube voltmeter that is portable, adaptable, and comparatively rugged and inexpensive can be built by using dry batteries to supply the necessary potentials, a zero to one-half milliammeter as the reading instrument, and a type '33 vacuum tube, which is a power output pentode used in battery-operated radio receivers. The low-reading meter, when used as a suppressed zero instrument, will give full-scale change for a potential change of about six hundred millivolts, which is a convenient range for many electrometric titrations.

A circuit for such an arrangement is given in Figure 1, and photographs of a complete voltmeter are shown in Figures 2 and 3. In this voltmeter, both plate and grid potentials are supplied from one forty-five volt dry battery, and the dry cells used to light the filament are also used to balance out the initial steady portion of the plate current.

The effective mutual conductance of this arrangement, which holds over a range of at least five volts on the control grid, is about 800 micromhos. The arrangement is quite stable; the random fluctuations are of the order of 10^{-8} to 10^{-7} amperes, and of course do not show on the meter used; drift is not noticeable after the batteries and tube have been aged for a few hours. The whole apparatus, including batteries, is mounted in a carrying case about 13 × 13 × 7 inches. The case could be made considerably smaller; this particular instrument was designed for student use and made so that the wiring and parts are easily accessible.

To adjust the voltmeter for a titration, the electrodes are put in the solution and connected so that the increasing negative (or decreasing positive) potential is applied to the grid. The battery switch S_1 is turned on (it must be turned on for a few seconds before S_3; otherwise only the bucking current flows through the meter while the filament warms up) and with the meter protected by setting R_3 to a low resistance, S_3 is turned on. Resistances R_1 and R_4 are then adjusted so that the meter reads the same whether S_2 is in position 1 ("titrate") or position 2 ("free grid"). R_3 is then carefully increased, with readjustment of R_1 if necessary, until full sensitivity is reached, when the meter is set at full scale with fine control R_2. S_2 is then thrown to the "titrate" position, and the titration

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started. This rather complex method of adjustment insures operation of the tube near its maximum input impedance and prevents the grid from swinging positive, attracting electrons, and causing appreciable current to be drawn from the electrodes. If the adjustment is made as outlined, the current through the electrode system will be less than 10^{-10} amperes.

As the titration proceeds, the meter reading decreases. The endpoint may be found from the readings, without converting to volts, either graphically or by the method of increments. More conveniently, and almost as accurately, the endpoint may be found by titration to the equivalence potential found in a preliminary rough titration. The endpoint may usually be estimated to a few hundredths of a milliliter, or nearly the accuracy of ordinary buret readings.

Several of these voltmeters have been in use for some time at Washington Square College as part of the laboratory equipment for the undergraduate course in physical chemistry. The students using them have been able to get reproducible and quite accurate results in various electrometric titrations, even with 0.01 N solutions or in the more difficult titrations. Figure 4 shows the results of a student's titration of ferrous sul-

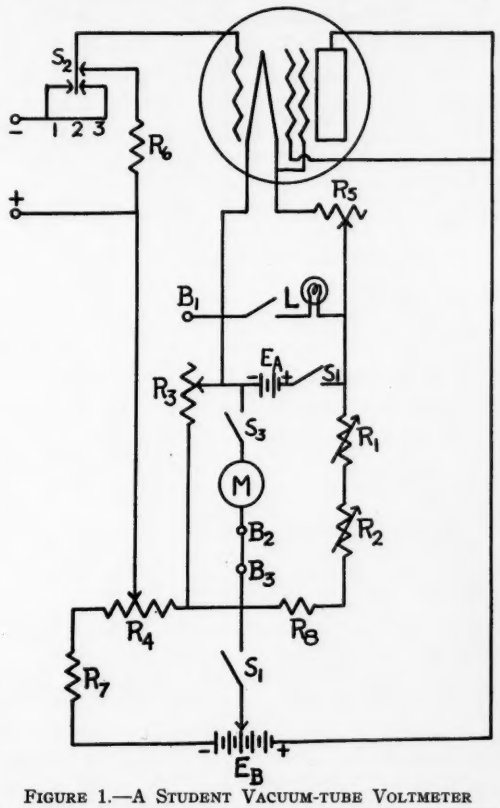

FIGURE 1.—A STUDENT VACUUM-TUBE VOLTMETER

S_1—Battery switch, double pole—single throw (Yaxley 740)
S_2—Grid switch, double pole—three position (Yaxley 762)
position 1 marked "Titrate"
position 2 marked "Free Grid"
position 3 marked "Voltmeter"
S_3—Meter switch, single pole—single throw (Yaxley 730)
R_1—Zero set variable resistor 0–5000 ohms (Electrad FB 554)
R_2—Fine control variable resistor 0–500 ohms (Electrad FB 551)
R_3—Meter shunt variable resistor 0–10,000 ohms (Electrad RI 240)
R_4—Bias control potentiometer 5000 ohms (Electrad FB 554)
R_5—Variable filament resistor 0–10 ohms (Electrad RI 204). Adjusted so that an ammeter placed in series with E_a registers 0.26 ampere. Readjusted occasionally.
R_6, R_7, R_8—Grid leak type fixed resistors
R_6—Grid leak, 10 megohms
R_7—Bias set resistor, 5000 ohms
R_8—Protective resistor, 50 ohms
V.T.—'33 type (RCA or Sylvania)
M—0–500 microammeter (Weston 301)
L—Pilot light with switch
E_A—Filament battery, two No. 6 dry cells (Eveready or Burgess)
E_B—45-volt B Battery, tapped at 22½ volts (Eveready 485, or Burgess 22308)
B_2,B_3—Binding posts to allow external use of a more sensitive meter
$B_3$$B_1$—Binding posts to allow microammeter to be used externally

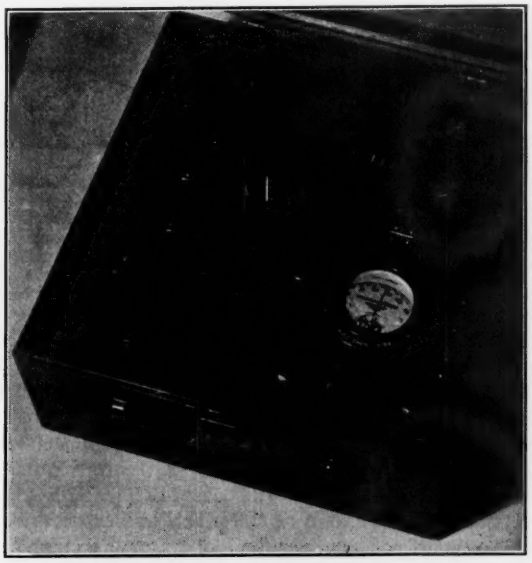

FIGURE 2.—A STUDENT V. T. VOLTMETER

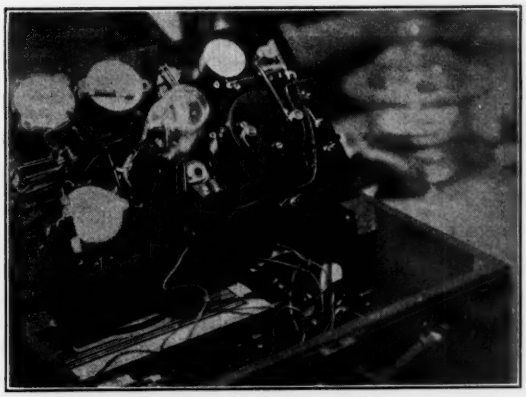

FIGURE 3.—A STUDENT V. T. VOLTMETER

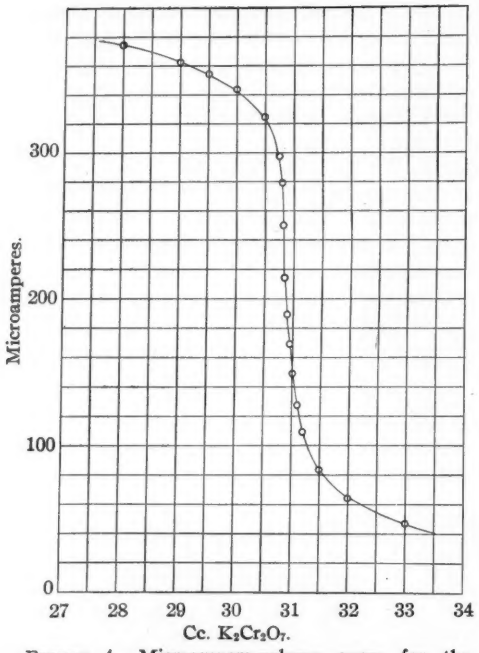

FIGURE 4.—Microampere-volume curve for the titration of ferrous ammonium sulfate with 0.10 *N* potassium dichromate solution.

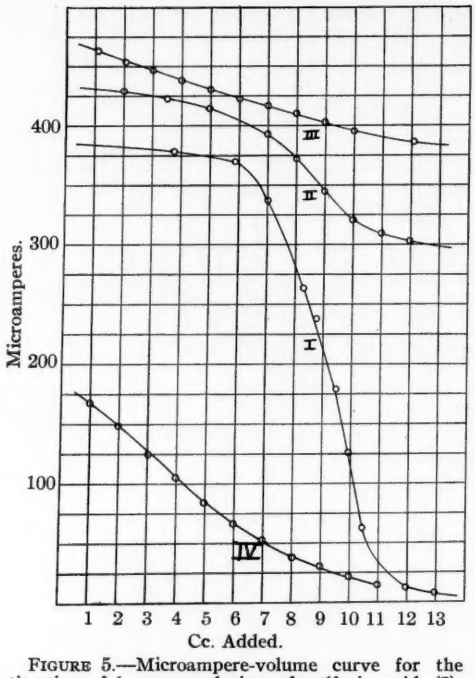

FIGURE 5.—Microampere-volume curve for the titration of benzene solution of sulfuric acid (I), acetic acid (II), and phenol (III), and prime kerosene distillate (IV) with 0.10 *N* alcoholic NaOH.

fate with tenth-normal potassium dichromate solution, using a silicon carbide and platinum electrode system (*1*). The accuracy that might be expected of the instrument can be estimated from this typical plot.

These voltmeters are, of course, limited in usefulness in a titration by the nature of the potential curve in the region of the endpoint, and by the resistance of the available electrodes. The first limitation applies to all potentiometric titrations, but vacuum-tube devices are notably useful with a high-resistance electrode system. As evidence of the adaptability of a voltmeter of this type, and of the practicability of having one as part of the regular laboratory equipment, titration curves taken in connection with a research problem in oil treatment are shown. Prime kerosene distillate from Conroe County crude was titrated with alcoholic sodium hydroxide, using a glass electrode and a saturated calomel half-cell (Figure 5, curve IV). The rather indeterminate results seem to indicate the presence of some amount of an acid, presumably a very weak one. But it seems entirely possible, considering the extremely high resistance of the nonconducting oil and of the glass electrode, that no better results could be expected no matter what the reagents. Consequently, the titration was repeated substituting for the kerosene known benzene solutions of sulfuric acid, acetic acid, and phenol (Curves I, II, and III, respectively, of Figure 5). By comparing the curves obtained, not only does the presence of an acidic substance seem to be established, but also an idea of its general nature has been gained. Whatever may be the real significance of titrations of this type, it suffices to point out that the titrations would have been impossible with the ordinary potentiometric technic.

Vacuum-tube voltmeters are, of course, not restricted to use with titrations. These voltmeters have been unexpectedly useful for general purpose measurements around the laboratory. Used with switch S_2 in position 3 ("voltmeter") they are stable and convenient low-reading voltmeters with a resistance greater than 10^7 ohms per volt. So, apart from their purely pedagogical value in familiarizing students with vacuum tubes and electrometric titrations, these voltmeters have proved worth while and have more than repaid the trouble taken to build them.

The authors realize that vacuum-tube voltmeters are not new, and in view of the evident simplicity of the arrangement described, it is hardly possible that even this is new. On the other hand, they feel that the description in a readily available journal of a convenient, portable, and rugged instrument constructed of inexpensive and easily obtainable parts is worth while, in that it may perhaps save the chemist unacquainted with all the details of electronic devices some little care and trouble in designing a comparatively simple instrument for his own use.

The authors wish to thank Mr. G. H. Symonds for permission to use the oil titration data.

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For a review of the literature dealing with potentiometric titrations and the application of vacuum-tube voltmeters see N. HOWELL FURMAN, "Potentiometric titrations, a review and a report of progress," *Ind. Eng. Chem., Anal. Ed.*, **2**, 213 (1930).

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MATHEMATICAL PROBLEM PAGE

Directed by EDWARD L. HAENISCH

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A FIRST-ORDER, first-degree differential equation which is linear with respect to y and dy/dx has the form, $dy/dx + Py = Q$, where P and Q are constants or functions of x alone. The solution of this equation has been shown by Leibnitz to have the form:

$$y = e^{-\int P dx}\left[\int Q e^{\int P dx}\, dx + C\right]$$

The reader has already obtained this formula for the case when P is a constant in the solution of Problem 4 of the March Page.

Bernoulli has shown that equations of the type $dy/dx + Py = Qy^n$ can be changed into the linear form by the following method:
Divide by y^n and multiply by $-(n-1)$,

$$-(n-1)y^{-n}(dy/dx) - (n-1)Py^{-(n-1)} = -(n-1)Q$$

Let $v = y^{-(n-1)}$ and $dv = -(n-1)y^{-n}dy$ or $dv/dx = -(n-1)y^{-n}\, dy/dx$

By means of this substitution the equation is reduced to a linear form in v.

$$dv/dx + (1-n)Pv = (1-n)Q$$

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MELLOR: 387
PARTINGTON: 226

PROBLEMS

1. Solve: (a) $xdy + (x+y)dx = 0$

   (b) $\dfrac{dy}{dx} + \dfrac{Ky}{a-x} = \dfrac{Kx}{a-x}$

   (c) $\cos^2 x(dy/dx) + y = \tan x$

   (d) $dy/dx + (2/x)y = 3x^2y^{4/3}$

2. Let an initial amount a of a substance A change into substance B, and B in turn change into C. Assume the reactions to be of the first order, *i. e.*, at time t when x mols of B and y mols of C have been formed:

$$dx/dt = K_1(a-x) \text{ and } dy/dt = K_2(x-y).$$

Obtain an equation for y in terms of the reaction rate constants, the initial concentration, and the time. (Hint: Solve the first equation for x and substitute the value in the second and solve.)

3. The rate of decomposition of a radioactive substance is proportional to the amount of substance present, *i. e.*, $dN/dt = -\lambda N$. When Io loses an α particle it is changed into Ra which in turn loses an α particle and becomes Rn. It takes 7.6×10^4 years for $1/2$ of an amount of Io to decompose and 1600 years for $1/2$ of an amount of Ra to decompose. If we start with 1 mol of Io how much Io and Ra will we have in 10,000 years?

4. The Helmholtz equation relating the impressed potential difference, E, and the current, i, in a circuit containing resistance, R, and inductance, L, is:

$$E = iR + L(di/dt)$$

Obtain $i = f(E, R, L, t)$.

SOLUTIONS TO MARCH PROBLEMS

1. The use of the factor $1/x^2$ gives $dy/x - y(dx/x^2)$, an equation which is exact and has for its solution, $y = Cx$. The factor, $1/y^2$, gives $dx/y - xdy/y^2 = 0$, the solution of which is $x = c'y$. The factor $1/xy$ gives $dx/x - dy/y = 0$, the solution of which is $\ln x - \ln y = C''$ or $x/y = e^{C''}$. The solutions are equivalent if $C = 1/C' = e^{-C''}$.

2. Multiplication by the suggested factor gives: $ay^{n+1}dy = 2ydy/x - y^2dx/x^2$. The terms on the right side of the equation constitute the exact differential of y^2/x. The integrated form of the equation is: $\dfrac{a}{n+2}y^{n+2} = \dfrac{y^2}{x} + C$.

3. (a) $(x^3 + 3y^2x)dx + (y^3 + 3x^2y)dy = 0$.
   $\partial M/\partial y = 6xy$; $\partial N/\partial x = 6xy$
   The equation is exact and gives upon integration:
   $\dfrac{x^4}{4} + \dfrac{3}{2}x^2y^2 + \dfrac{y^4}{4} = C$ or $x^4 + 6x^2y^2 + y^4 = C$.

   (b) Rearranging the terms: $ydx + xdy + xy^2dx - x^2ydy = 0$
   $d(xy) + xy^2dx - x^2ydy = 0$
   This form suggests the factor, $1/x^2y^2$.
   $\dfrac{d(xy)}{x^2y^2} + \dfrac{dx}{x} - \dfrac{dy}{y} = 0$
   $-1/xy + \ln(x/y) = C$

   (c) $ydy + ydx - xdy = 0$. Use the factor, $1/y^2$.
   $\dfrac{dy}{y} + \dfrac{dx}{y} - \dfrac{xdy}{y^2} = 0$. The last two terms are the exact differential of x/y. The complete solution is $\ln y + x/y = C$

   (d) $2xy^2dx + e^xydx - e^xdy = 0$. Use the factor $1/y^2$.
   $2xdx + \dfrac{e^xdx}{y} - \dfrac{e^xdy}{y^2} = 0$. The last two terms are the exact differential of e^x/y. The complete solution is
   $x^2 + \dfrac{ex}{y} = C$.

4. $dy - aydx = Qdx$.
   $e^{-ax}\, dy - ae^{-ax}\, ydx = Qe^{-ax}\, dx$

   The left-hand side of the equation is the exact differential of $e^{-ax}y$. The complete solution is: $e^{-ax}y = \int Qe^{-ax}\, dx + C$ or $y = e^{ax}\left[\int Qe^{-ax} + C\right]$.

ABSTRACTS

R. A. BAKER, *Abstract Editor*

A. T. BURTSELL
F. B. DAINS
TENNEY L. DAVIS
SPURGEON GAGE
J. HOWARD GRAHAM
B. CLIFFORD HENDRICKS

J. W. HOWARD
D. C. LICHTENWALNER

GRETA OPPE
C. M. PRUITT
LEOPOLD SCHEFLAN
E. D. WALTER
SIDNEY WEINHOUSE
G. H. WOOLLETT

KEEPING UP WITH CHEMISTRY

Distilling pine products at New Orleans. J. B. NEALEY. *Chem. & Met. Eng.*, **43**, 20–1 (Jan., 1936).—Tar, pitch, turpentine, and their derivatives are produced in the South by the dry or destructive distillation of pine wood. The residue is charcoal. Log trimmings and stumps are used. The longer this material has been on the ground the more valuable it is, as the outer portion has rotted away leaving the resinous heart.

The operation is carried out in horizontal steel retorts 5 ft. in diameter by 16 ft. long. Gas is the best fuel. The light crudes containing turpentine, pine oil, dipentene, and Laksol, come over first and are cooled in water condensers. The heavy oils come over last. The crude oils are redistilled and purified.

J. W. H.

Chemical trends in petroleum refining. B. T. BROOKS. *Chem. & Met. Eng.*, **43**, 10–3 (Jan., 1936).—The most significant fact about the petroleum industry during the last 15 or 20 years is that it makes use of nearly every branch of science—chemistry, metallurgy, physics, and geology, and the many engineering applications of these sciences. Parallel with this is the large amount of theoretical research on petroleum going on in various universities. Forty-one research projects are being carried out under the administration of the American Petroleum Institute.

The effort to produce motor fuel of high octane rating still continues, as does the search for organic compounds having high anti-knock value. The larger refineries are building larger units for cracking and distilling.

Better auto engine design has kept the consumption of lubricating oils from increasing as rapidly as gasoline consumption. A process for converting gasoline to Diesel oil would appear to be rational if and when Diesel automotive engines are more widely used.

There is no reason for hysteria concerning a possible shortage of petroleum occurring in about five to eight years. J. W. H.

Trends in the paint and varnish industry. W. R. FULLER AND M. S. ARMSTRONG. *Chem. & Met. Eng.*, **43**, 4–9 (Jan., 1936).—With more than 1000 American chemists and chemical engineers working on paints, varnishes, lacquers, and their essential raw materials, progress is being made at a rate which taxes the capacity for comprehension of those who are in the thick of it.

The use of synthetic resins is the outstanding development of recent years. Many new phenol-formaldehyde resins have been made available by the use of the aromatic substituted phenols. The alkyd resins are the chief center of interest today. By replacing the acids of non-drying oils with those of drying oils new air-drying resins have been developed. The vinyl type resins are in much demand for lining beer cans.

Two resin-like materials which show high chemical resistance have been derived from rubber.

The only oils of such quality and present availability as to merit attention as possible substitutes for linseed oil are soya, perilla, fish, and tung oils.

Pigment producers have been fully as active as resin producers in developing new products and countless modifications of established ones. Titanium pigments are the outstanding development in white pigments.

Water-emulsion lacquers are the most revolutionary developments. They have low cost, resistance to blushing, relative non-inflammability, and non-penetration of porous surfaces.

J. W. H.

Metallurgical trends of chemical engineering interest. C. E. WILLIAMS. *Chem. & Met. Eng.*, **43**, 17–9 (Jan., 1936).—It is no longer necessary to add alloys in making plain carbon steel of high and uniform quality. Nickel, chromium, molybdenum, and other materials are added to improve the corrosion-resistance and mechanical properties of steel. An alloy steel with 16% to 18% chromium and 0.10% or 0.12% carbon is the most useful of the stainless group. The 18% chromium and 8% nickel is also very popular. If 2% to 4% molybdenum is added to this steel it can be used for sulfite liquors, acetic acid, and zinc chloride. One-half of the nickel in the 18–8 type is often replaced with manganese—giving a steel good for drastic cold-working operations.

A recent development of much promise is the production of stainless-clad and nickel-clad steels, formed by welding sheets or rolling slabs of metals together. This is cheaper and often has better structural properties than the protecting metals themselves.

The use of 12% to 15% chromium steels marks the first real advance in securing satisfactory high-temperature properties under extreme conditions. The addition of titanium or columbium to plain chromium steels augments the resistance to oxidation at high temperatures and minimizes air-hardening tendencies.

The most interesting alloys in the non-ferrous field are those of 70% nickel and 30% copper to which aluminum and silicon have been added. They have high tensile strengths at elevated temperatures.

J. W. H.

A sulfurous chat. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **108**, 2–3 (Jan., 1936).—This article is an evaluation of the sulfur situation at the present time, for there have been in some quarters fears of future sulfur shortage and of shifting uses that may impair its industrial activity. The largest use for sulfur is for the manufacture of sulfuric acid, of which this country supplies 6 to 8 million tons a year. The fertilizer industry uses about a quarter of the sulfuric acid produced. Petroleum refining uses nearly a fifth. There are numerous sizable, though relatively minor, uses for the element, sulfur: heavy chemical manufacture, agricultural sprays, germicide in the poultry industry, paper making, vulcanization, and refrigeration. When public utilities are feeling better than they do now, sulfur-recovery systems may be used to transform their flue gases into sources of profit. Most of the elemental sulfur of the world is obtained from the sulfur domes of Texas and Louisiana. G. O.

Sorbitol and mannitol. J. R. FRORER. *Chem. Industries*, **38**, 57 (Jan., 1936).—Sorbitol and mannitol are hexahydric alcohols, and until now sorbitol has been a laboratory curiosity, quoted at $400 a pound, and mannitol available only as an importation. Now both are synthesized from corn sugar, and are available in tonnage quantities from their industrial sponsor, the Atlas Powder Company. A. T. B.

Aliphatics. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **108**, 1–2 (Jan., 1936).—Just as the coal-tar products created an enormous new industry, so the aliphatics now promise to follow a similar course. Enterprising chemists and firms have already found a bewildering variety of uses for some of them. The first economically successful synthetic rubber is made from an aliphatic compound, chloroprene. All of the anti-freeze compounds essential to winter motoring are aliphatic. The success of the brilliant and durable new paints, lacquers, and varnishes which have contributed so much to the appearance of American homes in recent years depends on the availability of a wide variety of aliphatic compounds. New basic aliphatics completely miscible with water have made possible the use of new dyes in the textile industry. Thus old industries are stimulated and new ones encouraged by the new and useful substances which become available. G. O.

Rubber in roads. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **108**, 3 (Jan., 1936).—Engineers and rubber men are watching with interest the possible use of rubber in road-building. One of the most irritating troubles with concrete roads is the present asphalt filler for expansion joints. It forces itself above the road level when it expands and does not recede properly when it contracts. Rubber latex compounds of a creamy consistency that vulcanize in two weeks to an elastic mass have been found to

overcome these difficulties of asphalt. A rubber latex cost of $1200 per mile for each lane of road is regarded as a net economy as compared with the labor costs on the maintenance of the present asphalt joints. G. O.

Chemically conditioned cold. ANON. *Ind. Bull. Arthur D. Little, Inc.*, **108,** 3–4 (Jan., 1936).—Gas refrigeration has been spoken of as one of the most important discoveries of this decade. This article explains the use of carbon dioxide and ozone as an accessory in the storage of food products and tells of the pioneer shipment of Australasian chilled beef into the British beef market, previously the monopoly of the Argentine. The presence of 10% carbon dioxide in the refrigerating chamber is capable of increasing the length of time which beef can be stored by 100%. Apples and other fruits can be conveniently stored in carbon dioxide of low concentrations. The gas also destroys the apple worm and makes the fruit keep longer after storage. Eggs and fish may be stored or shipped to advantage in chilled carbonated air. Mold spores are completely destroyed by an ozone concentration of 1.5 parts per million of air. Ozone also destroys odors, preventing the contamination of one type of food by another. Eggs may be preserved in a continuous concentration of 1 to 2 parts ozone for eight months and be as fresh as when first stored. In continental Europe ozonized "cooler" storage for meat is being used instead of "freezer" storage. In this country it has been tried on sausage-meat storage. Soft-skinned fruits are kept to advantage in ozonized air; but butter, bacon, fats in general, and mushrooms should be excluded from the ozonized chamber because of the off-flavors they develop. Ozonized refrigeration does not require the use of very tight rooms. Carbon dioxide and ozone do not react with each other; hence they may be used together to gain the extra efficiency. G. O.

General observations on the maple sugar situation. C. H. JONES. *Rept. New Eng. Assoc. Chem. Teachers*, **36,** 74 (Dec., 1935).—The production of maple sugar is confined to sections where rock and black maple trees are abundant, and centers around Vermont, New York, and Ohio—Vermont tapping about one-third of the approximately 16 million trees tapped annually. The yield per tree—1 pound poor, 2 pounds medium, 3 pounds good—is subject to variations, as the production depends upon weather conditions during March and April. Sap contains about 3% sugar; also mineral matter, organic acids, and traces of proteids. (About 28 gallons of sap are required for one pound of sugar.) Sucrose is the principal sugar that permeates maple wood, and the maple flavor which accompanies it gives to maple sugar its increased value over granulated sugar products.

Standard maple sirup weighs 11 pounds per gallon—has a sp. gr. of 1.32, a Baumé hydrometer density of 35–36, and boils at a temperature of 218°F. It contains not over 35% of water. National and state pure food laws require that maple sirup for retail trade weigh 11 pounds per gallon. This weight is desirable, as a thinner sirup would be likely to ferment, and a heavier sirup is likely to crystallize. Maple sirup is what might be called a crude product. No attempt is made to clarify it other than the skimming of the sap, and a simple sedimentation of the suspended malate of lime (niter) in the finished sirup. When samples are to be graded accurately it is necessary that they be free from niter. This can be accomplished by sedimentation or by filtration. S. G.

Chemistry of the sporting goods industry. A. S. MYERS. *Rept. New Eng. Assoc. Chem. Teachers*, **36,** 91 (Dec., 1935).—This address convinces one that an outstanding manufacturer of sporting goods does not employ hit-or-miss chemical methods. Instead "day-in-and-day-out" research secures the best possible results for his special field. Problems in rubber compounding need to be solved in order that tennis balls shall have certain required characteristics. Research in materials suitable for body and covering of golf balls, special methods of tanning leather, solution of problems arising from preparing steel used in golf clubs and gymnasium apparatus, are all a part of the chemist's task in this important industry. S. G.

HISTORICAL AND BIOGRAPHICAL

Salt—pioneer chemical industry of the Kanawha Valley. E. T. CRAWFORD, JR. *Ind. Eng. Chem.*, **27,** 1109–13 (Oct., 1935).—Salt was the pioneer industrial enterprise in this section, with its first crude furnace in 1797. In 60 years 160,000,000 lb. was produced annually.

The technic developed here in drilling salt wells was later applied to drilling for oil and to other industries. The manner in which early difficulties were overcome is told in an entertaining and instructive way in this and following issues. D. C. L.

ADMINISTRATIVE PROBLEMS AND DEVICES; CURRICULA

A free system of course selection. E. S. JONES. *J. Higher Educ.*, **6,** 418–24 (Nov., 1935).—Freedom from required courses in the Junior College, University of Buffalo, has resulted in fewer science selections by women and fewer language selections by men, in the tendency of all superior students to take more language and social-science courses, and in the choice of more courses in related fields and background subjects by all students. A. T. B.

Some educational bookkeeping. W. P. SHOFSTALL. *J. Higher Educ.*, **6,** 414–7 (Nov., 1935).—The Dean of Administration, Stephens College, tells of red tape, conservatism, and even stupidities which grow out of the too rigid following of rules of administrative procedure. A. T. B.

The selection of prospective teachers. P. V. SANGREN. *J. Higher Educ.*, **6,** 435–9 (Nov., 1935).—A centralized cumulative system of records combined with interrelated reports from a closely coördinated arrangement of student-personnel agencies forms the basis of this scheme of selecting prospective teachers. The proposer of this scheme is the Dean of Administration, Western State Teachers College, Michigan. A. T. B.

An introductory course. J. S. ALLEN. *J. Higher Educ.*, **6,** 410–3 (Nov., 1935).—The administrative background of the freshman survey courses at Colgate is described, and an account of the organization and a summary of the content of the Physical-Science Survey is given. This discussion is written by the Chairman of the Colgate Physical-Science Survey. Many topics such as sound, electricity and magnetism, quantitative analysis, etc., are purposely omitted in an attempt to organize a logically developed course in physical science, regardless of departmental barriers, and in order to give a part of it well rather than to attempt a general introductory course that would partially replace the usual elementary courses in each department. A. T. B.

A new general college. W. J. MATHERBY. *J. Higher Educ.*, **6,** 401–9 (Nov., 1935).—"While many features of our plan have been adapted from experiments and procedures found in, or tried out by, both American and European institutions of higher education, the University of Florida is the first state university to require all students to pass through the General College." The major phases of the program consist of a group of six comprehensive courses. One of the main purposes of the comprehensive courses is to present to the student, in the first two years, overviews of all the major fields of human activity before he is allowed to choose one of those fields for specialized study. In addition to the vocational and educational guidance afforded by the various comprehensive courses, more specific guidance is provided by a system of counseling and testing and by an elective comprehensive course which gives definite attention to a thoughtful presentation of the economic and social aspects of all vocations and professions. A. T. B.

Organic chemistry in the secondary school. H. McN. TURNER. *Rept. New Eng. Assoc. Chem. Teachers*, **36,** 72 (Dec., 1935).—The suggestion is here made that certain introductory organic chemistry be included in the general chemistry course. Points made in its favor include the possibility of linking it up with the regular course by using interest topics such as petroleum and gasoline, soil and air — plants — animals — air and soil, also illustrated by many so commonly used products as rubber, cellulose, lacquers, and textiles. S. G.

EDUCATIONAL MEASUREMENTS AND DATA

Universities and the crisis in education. B. T. BROOKS. *Ohio State Univ. Mo.*, Oct., 1935, pp. 19–20.—Dr. Brooks attributes the deaths of Prof. Jesse Day and Instructor Vilbrandt of Ohio State to overwork imposed by the economic conditions under which American universities are now struggling.

"It is a fair question to ask what the prospects for relief in this

situation are, not only for the sake of the faculty that is enduring it, but also for the sake of the students and for what we believe to be the real mission of the University. The question appears to be much graver than merely one of temporary economy.

"In America we are accustomed to think that higher education is popularly approved and supported. Yet, according to recent authoritative surveys, eight of the eleven most eminent American universities are supported mainly by private endowment and three are state universities. The nearly universal *opportunity* for higher education provided by American universities has been built up mainly by the active leadership of a few, and largely aided by the generosity of a few, who have believed in higher education, and not at all by a widespread popular insistence upon it.

"The Carnegie Foundation comments, in 1933, that the reasons given for the support of colleges and universities have often been vague or superficial, and that this possibly explains 'why unimpressed legislators and their taxed constituency have agreed to cut educational appropriations, while millions of dollars have been spent prodigally for highways, for duplicated governmental services and for life stipends to veterans with non-service injuries.' It has commonly been believed that one great reason for higher education was *social control*. Of this, certainly, there has never been greater need than now.

"It is possible that *American university standards* may have to be maintained by tax supported universities rather than by those supported mainly by endowments and gifts. In Europe many endowments and trust funds were practically wiped out by inflation. No one can now say with any assurance how far our own inflation will go. In 1933 the Carnegie Foundation (David S. Hill) in listing twenty factors of increased cost of higher education gave first place to 'changes in the value of the dollar.' Higher taxes taken out of the earnings of industry, and much of our reform legislation may make large private fortunes more difficult or impossible. It is proposed in pending legislation, not only to greatly raise inheritance taxes, which might stimulate bequests to university endowments, but it is also proposed to tax such bequests heavily.

"Some of the effects of the present situation on universities are already apparent. Tuitions and fees are generally higher and very probably will go much higher. In the ten years 1920–1930 the income of American universities and colleges from student fees increased 225.8 per cent., while the number of students increased 78 per cent. in privately supported institutions and a little less than 100 per cent. in publicly supported institutions. A survey made in 1932 stated, 'The earlier policy of free universities apparently is not sufficiently tenacious in the public mind to resist the growing cost in taxes. If the tax burden increases sufficiently, the tuition fee appears directly or in disguised form. If the tax burden becomes still larger, the total charge to the student increases still further.'

"The above remarks have been intended to show that this condition is not merely one of temporary economy. Alumni and faculty and trustees can do more than has been done to improve this situation. Budget paring is the Caspar Milquetoast method of solving the problem. Under prevailing conditions any university needs the most distinguished, active leadership, and also needs every bit of influence, moral support, and financial aid that its alumni can give to it." O. R.

The committee on testing. F. S. BEERS. *J. Higher Educ.*, **6**, 469–74 (Dec., 1935).—Since 1931, the Committee on Educational Testing has engaged in the business of helping teachers to a better understanding of their students, so that adequate provision may more readily be made for their development and guidance. To this end the Committee has recommended the use of comparable, comprehensive tests as the point of departure for the understanding of differences in ability and achievement. Such examinations are both difficult and expensive to construct; but fortunately, the American Council on Education has sponsored an organization devoted to compiling and standardizing subject-matter tests. These tests, which appear in comparable forms, one each year, cover the disciplines common to the senior high school and the junior college.

Hundreds of thousands of copies of the various tests recommended by the Committee have been used by schools and colleges for purposes of placement and diagnosis. The results have been interesting from many points of view. For example, it has been found that zero-order correlations obtain between age and achievement, that the relationship between length of training and achievement is often remote, that differences between schools are less striking than differences within a given college, that a high degree of overlapping exists from the freshman to the senior year in the same college. In a word, the results clearly call into question the unit and credit system which so long has been the heritage of American education, and they argue for some means of classification based upon achievement rather than upon the fulfilment of residence requirements and the satisfaction of an arbitrarily conceived pattern of course sequences. Several cases are cited to testify to the fact that these time-worn prescriptions must give way to more economical and humane practices.

As an instrument for educational guidance and as a means of helping the student to understand himself with a view to professional or vocational adjustment, the achievement test is probably superior to the general psychological test. A. T. B.

A coöperative project. A. C. EURICH. *J. Higher Educ.*, **6**, 480–7 (Dec., 1935).—The General College of the University of Minnesota was established three years ago. It was set up as an experimental unit to provide a general education for students whose needs were not being met adequately by other divisions of the University.

At the outset it was recognized that some provision must be made for constructing examinations for General College classes. Before the General College was organized, sixteen different studies in educational measurements at the college level had reached various stages of progress. It was a natural step, therefore, to extend the experimental study of examinations to the newly developed courses. Briefly, the steps followed at Minnesota are:

1. Formulation of the course objectives.
2. Formulation of the objectives for the comprehensive examinations.
3. Definition of each objective in terms of student behavior.
4. Collection of material for each course in terms of objectives such as vocabulary, facts, principles, illustrations, and problems.
5. The formulation of specific test items calling for student responses to measure each objective.
6. The evaluation, by the specialist in the field, of each test item in terms of subject matter and the objective being measured.
7. The administration of the tests to the students as short quizzes, mid-terms, or final examinations.
8. The evaluation of each test item in terms of its discriminative power. The total score on all items within a given section is used as the criterion for the evaluation of items within that section.
9. Determination of the reliability of each test.
10. The selection of test items on the basis of the discriminative power, objective, and subject matter for inclusion in the comprehensive examinations.
11. Further evaluation of items in the comprehensive examinations and of the total tests.
12. Filing, for further use, of test items under field and objective.

The administrative set-up devised to make the project a cooperative enterprise is an unusual feature of the plan. The preparation of each test involves the services of at least the following three and sometimes many more individuals: an instructor who is a specialist in the subject matter; a graduate assistant with considerable training and experience in the field in which he is to work; and an examination counselor, with not only some experience and interest in the field for which he advises, but also extensive training in the technics of developing educational and psychological tests. These three—the instructor, the test counselor, and the assistant—provide an organization for a research program in the development of examinations.

When the program was initiated three years ago, only one-half of the General College courses were incorporated within its scope. During the second year, a few additional courses were included. Now the plan is followed in all of the thirty courses offered by the General College during each term of the school year. Thus, throughout each quarter approximately thirty instructors, four examination counselors, and twenty-three examination assistants make the construction of tests one of their major problems. In addition, thirty Federal Aid students assist in the scoring and the item analysis of the tests. With this staff giving attention to an experimental project in developing examinations, the measurement program along with teaching becomes a major service of the College. A. T. B.

RECENT BOOKS

ORTHOHYDROGEN, PARAHYDROGEN AND HEAVY HYDROGEN. *Adalbert Farkas*, Dr. Phil. nat. (Frankfurt), Dr.-Ing. (Vienna). The Cambridge Series of Physical Chemistry. Cambridge: at the University Press; New York: The Macmillan Company, 1935. xiv + 215 pp. 47 figs. 13.5 × 21 cm. $3.50.

In 1926 very few people would have believed that the next six or eight years would produce enough new and radically different theoretical and experimental information about hydrogen—supposedly the best understood of all elements—to fill a volume such as the one here reviewed. In fact, if the author had included all there was to be said of heavy hydrogen this book would have been twice its present size. This work is a tribute to the rapid growth of our physical sciences.

The book is divided into two parts; Part I deals with ortho- and parahydrogen and Part II with heavy hydrogen. The subject matters of these two parts are not very closely related and each part is almost independent of the other. Part I begins with a very brief chapter on the salient facts which led to the discovery of ortho- and parahydrogen. This is followed by a chapter on the theory which led to the prediction that two forms of ordinary hydrogen existed and which allowed calculations to be made on the equilibrium between these two modifications. This theoretical portion deals with the relationship between nuclear spin and rotational quantum number (quantum mechanics) and also deals with the statistical treatment used in calculating the equilibrium involved. This section is followed by an observation of the thermodynamics, physical, and kinetic properties of these two modifications and a description of the experimental arrangement employed in the preparation and analysis. There is also a brief discussion of ortho and para systems of other molecules.

Slightly less than half the book is devoted to heavy hydrogen (Part II). Somewhat the same procedure in the presentation of the subject is adopted here as in the first part. The thermodynamic treatment is particularly emphasized. This part is not as complete as that on ortho- and parahydrogen but omissions here are to be expected because of the continued rapid development of this subject and its already great content. In both sections, however, the important developments are all adequately presented and in addition there is much factual material that may be used for reference (295 references are included).

As with any well-founded scientific article this book is not open to adverse criticism. The principal experimental facts and theories are simply and adequately stated—there is no room for argument. If one were forced to find criticism it might be said that an unduly small proportion of the book is devoted to heavy hydrogen.

Two Nobel prizes attest to the importance of the material here so well presented. The book is recommended to everyone desiring a more intimate knowledge of these latest developments in physical chemistry. However, the book is not recommended to anyone who does not have a solid foundation in this subject.

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DAS BUCH DER ALAUNE UND SALZE. (The Book of Alums and Salts.) A Source of Late Latin Alchemy, Edited, Translated, and Annotated by *Julius Ruska*. Verlag Chemie G.m.b.H., Corneliusstrasse 3, Berlin W. 35, 1935. 127 pp. 16.5 × 25 cm. Price bound, RM. 15.

Professor Winderlich's article (trans. Ralph E. Oesper) on "*Al-Razi*'s Influence on Occidental Chemistry," projected for a future number of THIS JOURNAL, will describe so well the general nature of the researches which Professor Ruska has been doing on *al-Razi*, and the place among them which is occupied by the Book of Alums and Salts, that it seems undesirable here to attempt to anticipate it. Ruska's work has greatly improved our knowledge of Muslim chemistry and has made clear the most important sources of the mediæval Latin chemistry which was derived from it.

The Book of Alums and Salts is an Arabic compilation based on the writings of *al-Razi* and *Jabir* and upon Alexandrian sources. It underwent various changes and additions by the Muslim chemists and existed in a number of versions before it came to the Latins—to whom it supplied what was perhaps their most important source of chemistry. It was known to Gerard of Cremona who translated it into Latin and supposed it to be the work of *al-Razi*. Vincent of Beauvais ascribed it to *al-Razi* and quoted extensively from a Latin version of it. A number of anonymous manuscripts of the translation are also known. Ruska points out that no Arabic original of the work exists among the known authentic works of *al-Razi*. He has made a careful study and comparison of the Latin Paris Ms. 6514, which bears the name of *al-Razi*, and the supplement, *De Mineralibus Liber*, of the *Compendium Alchemiæ* of John Garland which was printed at Basel in 1560—*Tractatus de Salium Aluminumque varietate, compositione et usu Scriptoris incerti* (Treatise of an unknown writer on the Variety, Composition and Use of Salts and Alums). He seems to have been the first to note the resemblance of the latter to the Book of Alums and Salts. In part the two are identical, and in part each contains material which is not contained in the other. They differ in the Arabic words which have been retained in the Latin, in the additions which have evidently been made to them, and in the characteristically Muslim and Christian references to God which have been retained or added as the case may be. They appear to be derived from two different earlier Arabic versions. Finally Ruska has discovered in the Berlin Ms., Springer, 1904, an Arabic original which agrees in part and differs in part from the Latin versions. His book presents the evidence clearly and convincingly. It contains the original Arabic text and the two above-mentioned Latin versions together with a German translation, which covers them all, with indications of the variants and identities.

The Book of Alums and Salts is a sincere compilation of the chemical knowledge of its time, without mystery and without nonsense. It is by no means limited to the materials indicated in its title but treats of the many substances which were used by the Muslim chemists, arsenic sulfide, sulfur, mercury, the heavy metals, minerals, etc., vitriol, alkali, glass, and the imitation of precious stones. Its exposition, naturally, is based upon the very serviceable theory which prevailed at the time, the sulfur-mercury theory which is associated with the names of *Zosimos* and *Jabir*. The book makes one realize that there were great chemists among the Muslims, and makes one suspect that there were no truly great ones after them in Europe until the time of Paracelsus.

Our thanks again to Professor Ruska for his fundamental contributions to the history of chemistry.

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QUALITATIVE CHEMICAL ANALYSIS (INORGANIC AND ORGANIC). *F. Mollwo Perkin*, Late Head of the Chemistry Department, Borough Polytechnic Institute, London. Revised by *Julius Grant*. Fifth edition. Longmans, Green and Co., London and New York, 1935. x + 377 pp. 13.5 × 21.5 cm. $3.50.

The first edition of this text appeared in 1901. Since that time the text has passed through several editions and printings. The present edition (fifth) has been enlarged by including sections on microanalysis (both inorganic and organic), organic reagents and spot tests, and some of the less common elements; and by treating in more detail some of the rarer elements and alkaloids.

The text is divided into two parts; the first considers inorganic substances, and the other, organic. The inorganic section is

composed of ten chapters, the first two of which contain instructions pertaining to dry reactions, micro methods, and reactions in solution. The latter is accompanied by a very brief discussion of some of the theoretical considerations of the properties of solutions. This is too brief to be of any value to the student, but he is referred to other texts for more complete information. Six chapters of Part I are devoted to the chemistry of the metal ions; one chapter to the chemistry of the acid ions; and the last chapter of this section, to the systematic examination, separation, and detection of anions and cations.

Part II contains eight chapters concerning the reactions of and tests for organic substances. In the first of these chapters methods for the detection of carbon, hydrogen, nitrogen, the halogens, sulfur, and phosphorus in organic compounds are considered. There then follows in the remaining chapters of Part II a discussion of the reactions and methods for the separation of organic acids and phenols, the reactions of esters, hydrocarbons, higher fatty acids, glycerides, aldehydes, alcohols, acetone, carbohydrates, bases, glucosides, and alkaloids.

The text is written from a practical viewpoint; it contains, for each substance, several tests which have been thoroughly checked by the author, and its value lies chiefly in the availability of tests for organic as well as inorganic substances. In these respects the text is an excellent reference for those engaged in analytical procedures. It could be used in courses designed to impart the practical methods of analysis; however, to be used in the average course of qualitative analysis it would be necessary to support it with a theoretical treatment of the properties of solutions, ionization and ionic equilibria, and oxidation and reduction.

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ORGANIC CHEMISTRY. *Howard J. Lucas*, Associate Professor of Organic Chemistry, California Institute of Technology, Pasadena, California. First edition. American Book Company, New York City, 1935. vi + 686 pp. 92 tables. 42 figures. 14 × 21.5 cm. $3.60.

This book is an interesting, modern text with a distinctive approach to the subject. The author has attempted not only to present the subject matter of organic chemistry in a systematic and logical manner, but also to correlate the material with fundamental principles of theoretical chemistry. Especial emphasis has been placed on: (1) class reactions, (2) relationship to inorganic compounds, (3) molecular structure, (4) energy relationships, (5) electrochemical characteristics, and (6) application of electronic theories.

After the customary introduction, the author takes up the question of valence, and points out the differences between ionogens and non-ionogens. Atomic structure, electronic distribution, and the electronic differences between the various types of bonds in ionic and non-ionic compounds are pointed out. The semi-polar double bond and the hydrogen bond are described. The principle of minimum kernel repulsions is used in order to decide on the arrangements of the atoms in the molecule. Tables of kernel repulsions and bond energies are given and the concept of resonance is discussed. The third chapter deals with the properties of ionic, non-polar, and dipolar substances and a correlation of these properties with chemical constitution. The succeeding chapters deal with the various classes or homologous series of organic compounds.

The outstanding characteristic of the book is the correlation of energy relationships with reactions. For example, substitution of paraffin hydrocarbons by the halogens is considered to parallel the reaction of the halogens with hydrogen. The decrease in free energy in formation of the hydrogen halides is a measure of the driving force of the reaction, and hence fluorine has the greatest tendency to react, whereas iodine has the least. The application of bond-energy values to substitution also aids in explaining the differences observed in substitution by chlorine, bromine, and iodine. The thermochemistry of the hydrocarbons is discussed and used in consideration of the cracking process. The differences in reactivity of single, double, and triple bonds is also correlated with the energy relationships.

These comments are sufficient to indicate the general tenor of the book. The use of these physico-chemical concepts and theories is not overemphasized, but is woven into an excellent discussion of the preparation and reactions of each of the classes of compounds, and such discussion aids greatly in gaining a clearer concept of the properties of the compounds. The presentation is not dogmatic, but discursive.

Numerous tables of organic compounds with their physical properties are given, and are a great aid in giving the student a working knowledge of the properties of the compounds. These ninety-two tables also add to the reference value of the book.

Some of the important methods for identifying and characterizing each homologous series are given near the end of the discussion of each class of compounds. Schematic charts showing important reactions and interconversion of organic compounds give the student an excellent review. Finally, at the end of each chapter, a set of questions and problems is given. These are excellent, and do much to get the student to think and reason rather than memorize.

The book is written in a smooth, logical style and represents an enormous amount of work. It is, quite evidently, the publication of material which the author has been using in teaching his own students for some time. Very few errors were noted, and these are not serious. The reaction between *n*-propyl magnesium bromide and carbon dioxide on page 169; the formula for chloral, page 256; and the statement on page 143, that allyl alcohol gives iodoform, are incorrect. The equations showing the formation of quinoline by the Skraup reaction (page 615) do not represent the actual sequence of reactions involved. The production of *n*-propyl and isobutyl alcohols by the carbon monoxide-hydrogen reaction should be included. Vitamins A and C are discussed, but not B_1, B_2, or D. In view of the importance of polymerization reactions, it would perhaps be desirable to expand the treatment for this process at appropriate points in the text. These comments are, however, minor, and the author has written a distinctly up-to-date, comprehensive text.

It is evident from the above comments that this textbook can be used with success only with students who have completed a year of physical chemistry (which emphasized thermodynamics and electronic structures) *before* beginning the study of organic chemistry. It should find use in schools and colleges where the teaching of physical chemistry precedes the teaching of organic chemistry. The book is an excellent one for graduate students. Its publication constitutes an interesting experiment in the presentation of organic chemistry, and the extent to which it will be used will be watched with great interest.

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SUGGESTIONS TO AUTHORS OF PAPERS SUBMITTED FOR PUBLICATION BY THE UNITED STATES GEOLOGICAL SURVEY, WITH DIRECTIONS TO TYPISTS. *George McLane Wood.* Revised and enlarged by *Bernard H. Lane.* Fourth edition. United States Government Printing Office, Washington, D. C., 1935. vii + 126 pp. 14.5 × 23 cm. Paper bound. For sale by the Superintendent of Documents, $0.15.

Although this pamphlet has been prepared specifically for Geological Survey authors, it is easy to see why authors outside the survey have found its suggestions invaluable and why seven reprintings of the preceding edition were necessary.

The first forty-eight pages deal chiefly with geological subject matter or with style practices that vary slightly among first-rate periodicals. Even this portion of the pamphlet, however, may be read (or at least skimmed) with profit by writers on other than geological subjects.

The section entitled "Suggestions as to expression" and the "Summary of the features of a good manuscript" (pp. 49–103) are heartily recommended to all writers of scientific or factual subject matter. The author and reviser have not hesitated to

quote literary critics, professors of rhetoric, and literate scientists in amplification of their own discussion. Much as the reviewer detests wall mottoes, and much as he should therefore hesitate to inflict them upon others, he would like to post a judicious selection of quotations on the study walls of many contributors to scientific journals. A few samples are presented here.

Adams Sherman Hill,[1] professor of rhetoric at Harvard University from 1876–1904 and afterward professor emeritus, gives the three following rules for good writing:

> 1. The rule of precision: Of two forms of expression which may be used in the same sense that one should be chosen which is susceptible of but one interpretation. Observance of this rule tends to give each word a meaning of its own.
> 2. The rule of simplicity: Of two forms of expression which may be used in the same sense the simpler should be chosen. The simpler a word or phrase the more likely it is to be understood, and simplicity in language, like simplicity in dress or manners, belongs to the best society.
> 3. The rule of euphony: Of two forms of expression which may be used in the same sense that one should be chosen which is the more agreeable to the ear. It is of course wrong to give undue weight to considerations of euphony, but when no sacrifice is involved it is desirable to avoid an expression that is unusually difficult to pronounce or to substitute for an extremely disagreeable word one that is agreeable to the ear (p. 52).

Anatole France[2] writes:

> A simple style is like white light. It is complex, but not to outward seeming. In language a beautiful and desirable simplicity is but an appearance, and it results only from the good order and sovereign economy of the various parts of speech (p. 53).

Concerning "proper repetition," Clifford Allbutt[3] is quoted.

> A notion is prevalent that the repetition of a leading word or words in a sentence or short period constitutes an offense called "tautology." In this false sense of tautology the mathematician might incur censure for the repetition of symbols in an equation. If the word first accepted be precisely the word wanted, to vary it is to vary the sense, to confuse the argument, and to vex the reader (p. 63).

Regarding the misuse of "cases" and "instances" Fowler[4] says:

> Case. There is perhaps no single word so freely resorted to as a trouble saver and consequently responsible for so much flabby writing.
> Instance. * * * There is some danger that, as writers become aware of the suspicions to which they lay themselves open by perpetually using "case," they may take refuge with "instance", not realizing that most instances in which "case" would have damned them are also cases in which "instance" will damn them. The crossing out of one and putting in of the other will not avail: they must rend their heart and not their garments and learn to write directly instead of in periphrasis (p. 69).

In further illustration of the unnecessary use of "cases" (and, we may add, as a pointed argument for economy of expression) the following original and edited passages are presented:

> In the great majority of cases where coal exists but has not been found to be workable it lacks one of three things—either quality, thickness, or accessibility.
> Most unworkable coals are deficient in quality, thickness, or accessibility (p. 70).

Other bugbears of the editor are discussed—among them: "along these lines," "former" and "latter," "a number," "this" and "these," "like" and "such as," "due" and "owing."

The section on "Grammatical errors and problems" (pp. 92–8) offers much sound counsel and is adequately illustrated by examples.

"Typographic style" (pp. 103–11), "Correction of proof" (pp. 112–6), and "Directions to typists" (pp. 117–20) are in part specific to geological subject matter and to the *Style Manual of the Government Printing Office*, but also contain much generally applicable advice.

In all humility the reviewer recommends this inexpensive pamphlet to authors. He intends to make constant use of his own copy and hopes in consequence to lead a better literary life hereafter.

OTTO REINMUTH

[1] HILL, A. S., "The principles of rhetoric," pp. 18–22, **1895.**
[2] FRANCE, ANATOLE, "On life and letters," trans. by A. W. EVANS, **1914.**
[3] ALLBUTT, CLIFFORD, "Notes on the composition of scientific papers," 2nd ed., **1923,** pp. 127–8.
[4] FOWLER, H. W., "A dictionary of modern English usage," pp. **54, 277, 1930.**

THE NEXT HUNDRED YEARS. *C. C. Furnas*, Associate Professor of Chemical Engineering, Yale University. The Williams & Wilkins Company, Baltimore, 1936. xiv + 434 pp. 14 × 21.5 cm. $3.00.

After visiting "The Century of Progress" the author decided to write a book on what we do not know in science. This book "is fundamentally interested in the discoveries yet unmade, the developments not completed, the things that must still be done before we can advance to any marked degree." The subject is discussed under the five headings of biology, chemistry, physics, engineering, and social consequences.

"In a plant that manufactures its own food, the carbon dioxide is taken in principally through the leaves and the water is sucked in principally through the roots. These two chemicals get together by simple diffusional processes and in the presence of light and chlorophyll they unite to form the familiar compound, formaldehyde. . . .So far, nature is ahead of men in this photosynthesis game and has the best catalyst on the market."

"The common cold costs our nation two billion dollars per year. The productive time lost because of colds amounts to about 100 million working days per year."

"The Eskimo is said to be shorter-lived than most races. He ages very rapidly and often becomes an old man at fifty. Perhaps this is due to overworked kidneys because of the high protein diet, perhaps it is caused by the severe climate. The strict vegetarian on the other hand, is generally considered to have less resistance to infections. . .with accompanying weakened digestive organs and a tendency toward diarrhea."

"A century and a half ago a sixty-year old American living in Massachusetts had an expectancy of life of almost fifteen years. Now, the sixty-year old male resident of Massachusetts has an expectancy of only a little more than fourteen years."

"Long ago quarantines entered politics. Idaho is very proud of the fact that it can raise apples in certain spots; but Washington also raises apples and wants to sell them everywhere, including Idaho. The sovereign rights of the states are not broad enough to enable Idaho to put up a state tariff against Washington apples; but there is nothing to prevent the imposition of a quarantine."

"Rayon has become a reasonably satisfactory material; but it has never been good enough to send silk off the market. In America, at any rate, silk consumption has gone up during all the ascendancy of rayon."

"In this most horsepowered of all eras we have made but two fundamental advances over primitive man. We have invented the steam engine and the water wheel. We still depend upon the methods of a very temperamental and insufficient terrestrial nature to supply our demands for calories and B.T.U.'s."

"There has never been an American light car that was built with an eye for the best possible quality; but there is no reason for this except the whims of the market. The light car has always been the cheapest car. We Americans seem to buy by the pound rather than by potential mileage."

"The farm is a vast organic chemical factory; but there are people who still judge the time for planting by the phases of the moon. For that matter, there are those who feel that the salvation of agriculture resides in politics instead of science and engineering."

WILDER D. BANCROFT

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A BRIEF COURSE IN QUALITATIVE CHEMICAL ANALYSIS. *Louis J. Curtman*, Professor of Chemistry, College of the City of New York. The Macmillan Company, New York City, 1936. viii + 249 pp. 13 figs. 15 × 22 cm. $2.25.

In the preface the author states that "this book contains com-

prehensive material for a one-semester course in qualitative analysis. Theory and laboratory work have been closely coördinated to provide a sound scientific foundation for the prospective student of chemistry, medicine, dentistry, agriculture, and engineering."

Part I comprises 70 pages and is devoted to the discussion of Theory, which is handled thoroughly and adequately. It would seem that possibly an unnecessary amount of space and attention is taken up with these theoretical considerations if any previous training in chemistry has preceded the use of the book. However, no adverse criticism is offered.

Part II, 50 pages, is taken up with the Reactions of the Metal Ions and of the Acids or Anions. This is also a satisfactory treatment of the subject matter, especially the statement of the conditions under which the reactions take place and the solubility of the products formed, etc. One omission was noted on page 109, where the best conditions for the reaction between nickel salts and dimethylglyoxime were not given.

Part III, 60 pages, on Laboratory Work, takes up the analytical processes, and this is an excellent piece of work. The directions are full and the reasons for the various steps are given with remarkable clarity. Doubtless one reason for this is the fact that the author has given much time to the study of the processes of qualitative analysis, as his many papers along these lines of investigation show. The reviewer has yet to see any book on this subject which excels in this particular.

Possibly a few slight criticisms are in point. It would seem that hydrocyanic, ferrocyanic, and ferricyanic acids should not be omitted and thiocyanic acid be the only member of this quartet included. The test for nitric acid seems somewhat inadequate considering its importance. On page 170 the reference to the precipitation of rubianic acid under Reaction 4 Cadmium seems to call attention to an omission. On page 180 the fact that a paper filter may reduce permanganic acid is not mentioned.

While the author states in a footnote on page 77 that the student is referred to other texts for a study of the rarer elements, the reviewer cannot but feel that any text which omits a certain number of these must often involve the student in serious analytical difficulty. The time has come when such elements as, for example, Be, Ce, Ti, V, Ta, Mo, W, and Se are no longer so rare as not to be met with frequently; and a statement as to how they may affect the analytical procedures becomes almost necessary if the object is to teach one how to make a qualitative analysis. As a treatise on the analytical method the book is excellent and its treatment of the limited field of the more common elements is worthy of high praise.

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THE CHEMCRAFT RUBBER CHEMISTRY MANUAL. *Jermain D. Porter*, Cornell University. The Porter Chemical Co., Hagerstown, Md., 1935. 77 pp. 12 × 20 cm. Paper-bound, $0.50.

Chapter I, "The World Discovers Rubber" (pp. 10–9), tells of the early history of rubber knowledge and, in some detail, of the experiments of Charles Goodyear. Chapter II, "How We Get Our Rubber" (pp. 20–8), describes modern plantation rubber growing and the gathering and treatment of the latex. Chapter III, "What Rubber Is and How It Is Used" (pp. 29–44), discusses the properties of rubber in the light of modern physical and chemical knowledge, but in simple language, and includes directions for the performance of numerous experiments. The titles of Chapters IV, "Making Tires" (pp. 45–56), V, "Wearing Apparel" (pp. 57–61), and VI, "Bathing Caps, Fire Hose, and Other Things" (pp. 62–71), are sufficiently indicative of their contents. Chapter VII is devoted to a discussion of "Sulfur" and to directions for experiments illustrating the chemical and physical properties of the element.

In all, the booklet contains directions for fifty-two experiments. A price list of materials and equipment for experimental use is included.

OTTO REINMUTH

ORGANIC CHEMISTRY. *F. Sherwood Taylor*, Ph.D., M.A., B.Sc., Assistant Master at Repton School. William Heinemann Ltd., London, 1933. Chemical Publishing Co. of N. Y. Inc., exclusive agents in North and South America. xii + 586 pp. 14 × 22 cm. 56 figs. $6.00.

This organic chemistry is "new" only in the sense that it has been recently brought to this country for distribution; it was first published in 1933, and apparently has not been revised or brought out in a second edition.

It is the claim of the author that "the chief novelty. . .of the book lies in the treatment of the carbohydrates as cyclic compounds." Certainly there was nothing novel in such a treatment as late as 1933.

The book provides a fairly complete survey of organic chemistry with rather more emphasis on alkaloids, carbohydrates, terpenes, proteins, and plant pigments than one would expect in a volume of this size. These sections are well done with the object of offering additional material for the medical student. This end is attained, but other more elementary subjects are not so adequately treated. Olefins, di-olefins, and acetylenic hydrocarbons are dismissed in about twenty pages, of which three are devoted to laboratory experiments. The discussion of alkaloids and plant pigments, on the other hand, occupies thirty-seven pages. Such important processes as the preparation of ethanol and other alcohols from olefins, and the polymerization of acetylene to vinyl acetylene and of the latter to a rubber substitute, find no mention, but we learn on an earlier page (p. 69) that isopropyl alcohol "is usually prepared by reducing acetone with sodium amalgam." Such a statement, without qualification, leaves the student in this country at least, with an entirely erroneous impression.

On page 68 we read, "The chemical properties of primary alcohols closely resemble those of ethyl alcohol. With the exception of isopropyl alcohol, they do not, however, give the iodoform reaction." The thoughtful student studying this statement will wonder whether his conception of primary alcohols is wrong, or whether the author means that all alcohols other than isopropyl alcohol and ethanol do not give the iodoform test. Isopropyl alcohol is not a primary alcohol, nor is it the only alcohol other than ethanol which responds to the haloform test.

Numerous laboratory experiments are described, illustrating the preparation and properties of important compounds. These experiments follow the discussion of the compounds to which they refer. The book is intended, therefore, to serve as a combination laboratory manual and textbook. By far the majority of the figures describe apparatus used in preparations, in analytical work, or molecular-weight determination.

The first thirty pages are devoted to a very complete discussion of qualitative and quantitative analytical procedures and methods of molecular-weight determination. The treatment of these subjects is far more extensive than one would anticipate in a book of this character.

A student who has learned that phosphorus pentachloride converts aliphatic primary alcohols into chlorides with fairly satisfactory yields will doubtless be disappointed when he tries the same reaction on phenol after reading "chlorobenzene can be prepared by the action of phosphorus pentachloride on phenol. . ." Some qualifying statement as to the unsatisfactory yield of chlorobenzene should be given. No mention at all is made of the preparation of phenol from chlorobenzene.

Aside from the eight errors in formulas or context noted at the beginning of the book, we were able to find only two others which were not self-evident. The formula of purine (p. 313) and that of etioporphyrin (p. 550) are incorrect.

After a rather careful reading of the text, we believe that the author has attempted to include in a relatively small book too complete a survey of the very broad subject of organic chemistry, with a consequent lack of attention to accuracy of detail. The result is a rather unbalanced volume which contains some chapters of a high degree of excellence and others which are decidedly mediocre. Print and paper and binding are excellent.

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